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**Infrared
Spectroscopy
Applications in
Organic
Chemistry**

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GH. D. MATEESCU

Infrared Spectroscopy

Applications in Organic Chemistry

Translated by Ludmila Birlădeanu

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To the memory of
Professor COSTIN D. NENITZESCU

FOREWORD TO THE ENGLISH EDITION

Molecular spectroscopy holds a unique place in the hierarchy of the science. Though basically a branch of physics it is a handmaiden of chemistry. Our classification of Science into a subset of sciences may be an aid and comfort to university administrators, but it creates artificial barriers to the interpretation of the physical world. Those of us who are concerned with the practice and teaching of vibrational spectroscopy in the chemical field are aware of the wide disparity between the approach of the chemist and the physicist to this subject. This is not the place to analyse these differences in depth, but it is appropriate to point out that the physicist is free to select from the whole field of chemistry those molecules that most effectively demonstrate his theoretical concepts whereas the chemist must develop interpretative procedures that are applicable to all molecules irrespective of structure, size, or symmetry.

A textbook of infrared spectroscopy for chemists must, in the first place, equip the student with the means to analyse and evaluate the spectra of all kinds of molecules he may encounter in the course of his professional work.

However there is a danger that it may degenerate into a mere compendium of facts if it does not at the same time lead the student through the more rigid disciplines of spectroscopic theory. Dr. Avram and Dr. Mateescu have demonstrated singular skill in their ability to tread this double path.

To those who are already familiar with the textbook literature of this subject, it is refreshing to discover the wealth of new illustrative material which the authors include in this text. Much of this is clearly recognizable as originating in the Laboratories of the Romanian National Academy of Sciences at Bucharest. The Romanian edition carried a Foreword by the late Professor C. D. Nenitzescu, and his pride and enthusiasm for the work in chemical spectroscopy carried out by the authors in his laboratory is evident there. It is deeply to be regretted that Professor Nenitzescu did not live to see the appearance of this English language version of the book. Under these sad circumstances this monograph also serves as a testimony of the outstanding work in chemical spectroscopy carried out under his guidance.

R. NORMAN JONES

Ottawa, August 11, 1970

FOREWORD TO THE ROMANIAN EDITION

Modern chemistry relies more and more on physical methods for investigation of structural theories and reactivity of substances, as well as for purity control in chemical industry. In this respect it is very different from the chemistry of the past century. We must acknowledge the great achievement of the physicists in providing methods for the solution of chemical problems. We also must acknowledge the achievement of a specialized industry for providing a large number of chemists with complicated but standardized instruments, enabling the performance of delicate physical measurement that required a high degree of specialization and costly equipment several decades ago.

It is the duty of the chemist to apply physical methods along with classical chemical methods both in fundamental and industrial research. It would be a great mistake not to take advantage of the methods and equipment provided by physics and industry and to rely solely on old-fashioned and cumbersome chemical methods. Each researcher or research group must apply the best available methods to the solution of problems in order to solve them in the shortest possible time and with the greatest efficiency. Therefore the researcher must not be confined to his own limited field but must learn the methods that will help him solve his problems, whether these methods be physical, chemical, mechanical or biological. In this respect the present book will be of help to chemists.

This book is not a book of physical chemistry. It is a book of organic chemistry because it is written primarily for organic chemists. The analysis of substances by means of infrared spectroscopy is one of the most efficient methods of investigation offered by physics to chemistry in the last decade. It is as necessary in basic as in industrial research.

This tool is the result of a collaboration between one of our most experienced spectroscopists and an organic chemist well known both nationally and internationally. We are grateful to the authors who put aside their research for a period of time and devoted their time and energy to offer organic chemists rich material systematized according to the principles of modern organic chemistry, and to present the most important results published in the literature from a critical point of view based on their long personal experience.

PREFACE TO THE ENGLISH EDITION

The size of this book has been reduced slightly in comparison with its original version. This is because we felt that the chapters dealing with infrared instrumentation and techniques could be deleted. We have made several improvements and additions to the remaining text.

Once again we wish to thank Dr. Gerhard Herzberg for his encouragement.

We are grateful to Dr. R. Norman Jones for his useful comments, especially with regard to the photometric definitions and nomenclature.

A special acknowledgement is due to Dr. Ludmilla Birlădianu for accomplishing the difficult task of the translation.

We also thank Dr. Charles Jewell who carefully read the manuscript, made many useful observations, and contributed to the authentic Americanization of the book.

Finally we thank the publisher for his kind patience toward difficult authors who are too busy to spend (regularly) their time with the meticulous work of reediting a book.

THE AUTHORS

PREFACE TO THE ROMANIAN EDITION

The importance of infrared spectroscopy is obvious from its applications in a variety of fields such as chemistry, physics, biology, pharmacy, medicine, geology, space science, astronomy, etc. Of these, organic chemistry is certainly its greatest beneficiary, both in basic research and in industry. This can be seen from the tremendous number of publications that have appeared in recent years.

The scope of this book is to provide the reader with sufficient understanding of the basic principles enabling him to apply the method to the solution of current problems in organic chemistry.

In order to meet this objective, the book is divided into three unequal parts. The first and the second parts were designed to be of introductory character, hence are relatively short. They are intended to provide the reader with the theoretical and technical background necessary for a complete and useful understanding of the third part, which is the main section of the book.

A brief outline of the theory of infrared spectra is given in the first part of the book. The systematization and symbols used are those of Professor Gerhard Herzberg's classical treatise *Molecular Spectra and Molecular Structure*, Vol. I and II (Van Nostrand, Princeton, New Jersey). The presentations are mainly qualitative. Details are given only when absolutely necessary for a clear understanding of the principle under consideration. In other words an attempt is made to maintain a balance between a complex theoretical treatment and a correctly simplified presentation accessible to a large number of readers. However, we considered it necessary to present the elementary notions on a higher level than commonly used in similar works on applied spectroscopy.

Only principles essential to our goal are treated. Important but not absolutely necessary topics (such as the theory of band intensities and the applications of group theory) are described briefly and qualitatively.

We try to present a clear image of the notion of group frequency by correlating qualitative aspects with the theoretical background.

The second part of the book deals with the theoretical and technical aspects of the infrared instrumentation and techniques. This part is mainly intended to provide the reader with the basic knowledge necessary for operating an infrared spectrometer after a relatively short period of training.

The third and main part of the book deals with a brief description of the various applications of infrared spectroscopy, such as identification, purity control,

and quantitative analysis; these are followed by a detailed presentation of infrared spectra of organic compounds based on the latest literature and on our own data.

The material is systematized according to functional groups with particular emphasis on correlations between chemical structure and infrared absorptions of the compounds under consideration. The spectra are presented in an order corresponding to the chemical classification of substances proposed by Prof. C. D. Nenitzescu in his well-known treatise of Organic Chemistry.

The most detailed chapter is that dealing with hydrocarbons, the fundamental compounds of organic chemistry. In chapters dealing with monofunctional compounds (halogen compounds, alcohols, phenols, ethers, organic sulfur compounds, organic nitrogen compounds, etc.) or bi-, tri- and polyfunctional compounds (aldehydes, ketones, carboxylic acids and their functional derivatives, derivatives of carbonic acid, etc.), we emphasize the significance of band positions and band shifts of the corresponding chemical bonds with respect to the electronic structure of these bonds. We point out the correlation of inductive and conjugative effects with band position and intensity, and treat hydrogen bonding extensively. We also stress the effectiveness of the method in conformational analysis and in various problems of steric configuration. Finally, we discuss two classes of natural products, carbohydrates and proteins, as well as aromatic heterocycles. Organic derivatives of phosphorous, arsene, silicon, and organometallic compounds have been omitted for lack of space.

In each instance we try to define the limitations of the method and to stress the point that reliable results can be obtained only by correlating infrared data with data obtained by other methods, such as Raman spectroscopy, nuclear magnetic resonance, mass spectrometry, etc.

The first appendix contains a table of characteristic absorptions for various classes of compounds, and the second appendix, the principal collections and catalogs of infrared spectra.

We wish to thank Prof. C. D. Nenitzescu for his encouragement, understanding, and support.

We are grateful to Prof. G. Herzberg (Ottawa) for his encouragement and his permission to use some figures and examples of his well-known monograph on infrared and Raman spectra.

We thank Prof. R. Mücke (Freiburg in Breisgau), Prof. H. W. Thompson (Oxford), Prof. Jean Lecomte (Paris), Prof. Marie-Louise Josien (Paris), Prof. Jean Lascombe (Bordeaux), Prof. D. Hadži (Ljubljana), and Prof. R. Norman Jones (Ottawa) for permitting us to use both their published and unpublished results.

We are grateful to our colleague, I. G. Dinulescu, for his assistance with the art work and proof.

THE AUTHORS

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INTRODUCTION

Infrared radiations were discovered by Frederic William Herschel in 1800. In an attempt to establish by temperature measurements the partition of radiation power in various regions of the solar spectrum Herschel observed that one of the reference thermometers placed outside the visible region beyond red showed the highest temperature (Fig. 1-1). Thus the existence of invisible radiations characterized mainly by their thermal properties was pointed out for the first time. These radiations were called thermal radiations^{*} because of their subjective physiological action and the fact that infrared sources are strongly heated objects. However, this term is inadequate since any electromagnetic radiation, visible, ultraviolet, and even X-rays, is transformed mainly into heat when absorbed by various substances. The effect is stronger in the infrared region because the highest energy emitted by common sources (incandescent bodies) lies in this region of the spectrum^{**}.

Thirty five years later Ampere recognized that infrared radiations undergo reflection, refraction, interference, and polarization similarly to visible light. However, infrared radiations have longer wavelengths.

The wavelengths in the infrared region are generally measured in microns μ ^{***}. The frequency of the vibrations is given by the relation

$$\nu = \frac{c}{\lambda}, \quad (0-1)$$

where $c = 2.99776 \cdot 10^{10}$ cm sec⁻¹ is the velocity of light in vacuum (ca. 3×10^{10} cm sec⁻¹). The frequency is measured in Hertz (Hz)^{****}.

* The name infrared seems to be due to Bequerel (1869), as opposed to ultraviolet, first mentioned by Stokes in 1852.

** For example, if we watch (in the dark) a silicon carbide rod being heated by an electric current of increasing intensity, we can sense thermal radiation long before seeing the rod. The eye, accustomed to darkness, can perceive visible radiation only when the temperature of the rod exceeds 500°C. As the temperature continues to rise, the object becomes brighter passing from dark- to light-red, to light yellow, and finally to white. At this point the temperature is about 1500°C. The maximum energy emitted by the rod lies in the infrared region.

*** $1 \mu = 1$ nm (nanometer) 10^{-3} mm 10^{-4} cm 10^3 m $\sim 10^4$ Å.

**** Hz = 1 period/second 1 sec⁻¹.

Radiation with a wavelength of 10μ (medium infrared) has a frequency of 3×10^{13} Hz. To avoid such large numbers the *wave number* (number of waves per cm) ν or $\tilde{\nu}$ is generally used. It is proportional to the frequency and to the reciprocal of the wavelength measured in a vacuum. It is expressed in cm^{-1}

$$\begin{aligned}\nu [\text{cm}^{-1}] &= \frac{1}{\lambda [\text{cm}]} \\ &= \frac{10000}{\lambda [\mu]} \quad (0-2)\end{aligned}$$

From (0-1) and (0-2) it follows that

$$\nu = \frac{c}{\lambda} = \nu' \quad (0-3)$$

Thus a wavelength $\lambda = 10\mu$ corresponds to a frequency ν of 3×10^{13} Hz and a wave number ν of 1000 cm^{-1} . The number of waves per cm is often used as a measure of the frequency. One says for instance that the symmetric stretching vibration of the CH_2 group has a frequency of 2853 cm^{-1} .

However the expression wave numbers should not be used for the unit cm^{-1} (for example) it is incorrect to say 1000 wave numbers instead of 1000 cm^{-1}).

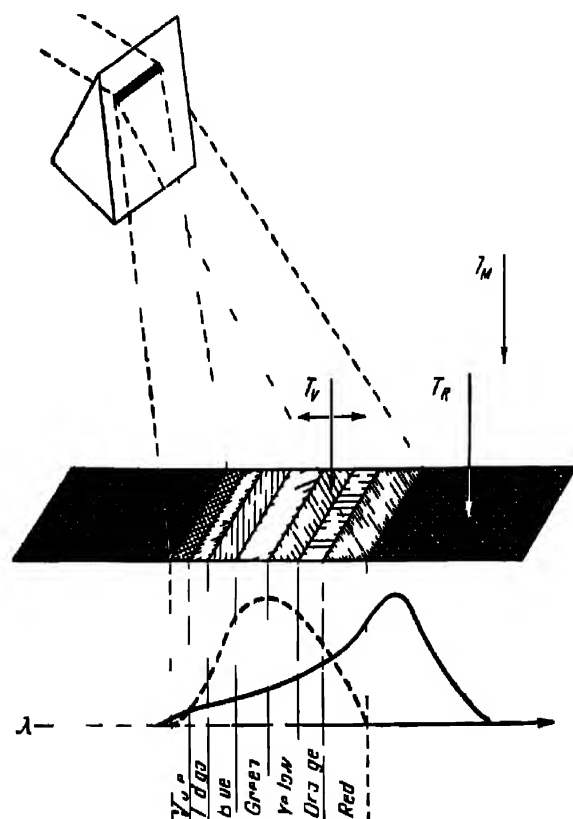


Fig. 1-1 Herschel's experiment

T_V — thermometer in the visible region, T_M — thermometer in the infrared, λ_M — reference thermometer. The curves show the approximate sensitivity of the human eye (dotted line) and the relative temperature elevation (solid line).

The velocity of light varies with the refractive index of the propagation medium, whereas the frequency is constant, consequently, the wavelength and wave number of electromagnetic radiation have different values in different media. The correction for values measured in air (ν_{air}) compared to those measured in a vacuum (ν_v) is extremely small and irrelevant for current work, for $\nu_{air} = 500 \text{ cm}^{-1}$ the correction $\nu_{air} - \nu_v = 0.13 \text{ cm}^{-1}$ and for $\nu_{air} = 5000 \text{ cm}^{-1}$, $\nu_{air} - \nu_v = 1.30 \text{ cm}^{-1}$.

According to the fundamental Planck-Einstein relation, the energy E is given by

$$E = h\nu' = h\nu c,$$

where h is Planck's constant $= 6.6249 \cdot 10^{-27}$ erg. sec. Therefore in spectroscopy one takes the wave number as a measure of the energy: $1 \text{ cm}^{-1} = 1.9861 \cdot 10^{-16} \text{ erg} = 1.2398 \cdot 10^{-4} \text{ eV} = 2.8590 \cdot 10^{-3} \text{ kcal/mole}$.

For a long time, it was difficult to make wavelength measurements in the infrared because of the lack of adequate detection means. Construction of very sensitive receivers and discovery of efficient methods of investigation enabled the detection of infrared radiations with very long wavelengths. On the other hand, by using electric oscillators one can produce radiowaves with wavelengths of the same order of magnitude. By progressive reduction of the radio wavelengths one can find the same radiation properties as those encountered by progressive enhancement of the infrared wavelengths and vice versa. The existence of an intermediate (overlapping) region between infrared and radio waves completes the entire picture of the electromagnetic spectrum, from

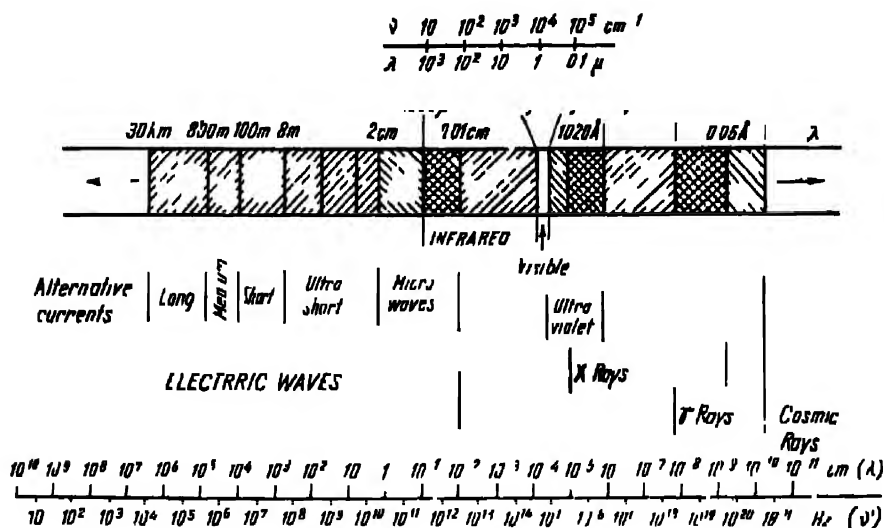


Fig. I-2 The electromagnetic spectrum

very short (0.005 Å) wavelengths, corresponding to emissions of radioactive bodies, to wavelengths of thousands of meters, corresponding to radio-waves.

The lower limit of the infrared region (next to the visible region) in the electromagnetic spectrum (Fig. I-2) was set at 0.76μ , using as a criterion the sensitivity of the human eye. As shown, the upper limit (which is difficult to

define) has wavelengths of the order of hundreds of microns. It is a vast region, including ca. ten octaves* as against four for the ultraviolet and less than one for the visible region.

The energies of radiations belonging to the first octaves in the infrared region are of the same order of magnitude as rotation and vibration energies of molecules (ca. 0.002–1.25 eV). Consequently, strong interactions of infrared radiations and matter are to be expected; for example, when a beam of infrared radiation of a certain frequency hits a molecule, two situations can exist. If the vibrations of the molecule differ in frequency from those of the incident radiation, no interaction takes place. However, if the molecule vibrates with the same frequency, it can absorb (under certain conditions) a certain amount of energy and rises to a higher energy level (excited state). This transition is discrete (quantized) and results in an increase in the amplitude of the vibrations. The absorbed energy is the difference between the energies of the two levels. It can be measured by means of various spectrophotometric devices. The latter phenomenon is called absorption by resonance**. It is responsible for the analytical use of infrared spectroscopy in physics, chemistry, and all sciences based on the knowledge of physico-chemical processes (medicine, pharmacy, biology, the corresponding industries etc.). By plotting the energy absorbed by a substance against frequency or wavelength, one obtains the absorption spectrum of that substance. Such absorption spectra, rather than emission spectra, are widely used in organic chemistry.

Classical electrodynamics and modern quantum theory show that the interaction of radiation and matter, resulting either in absorption or emission of energy, is possible only when a *dipole moment* variation is involved. Consequently, only vibrations or rotations of the molecule resulting in a change in dipole moment are *infrared active*. All the other vibrations or rotations are *infrared inactive*. Some of them can be observed by Raman spectroscopy*** which is an important implementation of infrared spectroscopy.

Molecular spectra enable the direct derivation of discrete energy levels of a molecule. From these levels one can obtain detailed information about the motions of electrons and nuclei in the molecule. The study of electronic motions provides the theoretical background for the understanding of chemical valence. From the vibrational frequencies one can calculate with great accuracy the forces between the atoms in a molecule and the heat of dissociations of molecules. From the rotational frequencies one can calculate very accurately internuclear distances and obtain accurate information about molecular geometry. Together with other new methods (e.g., microwave spectroscopy, nuclear mag-

* One octave—a notion used mainly in acoustics—is a range of frequencies (or wavelengths) where the upper limit differs from the lower one by a factor of two.

** The vibrational energy absorbed by a molecule is transformed into translational energy on collision with a neighboring molecule. The excited molecule returns to its initial state and is capable of a new absorption. Translational energy results in the generation of heat. Consequently, on absorption by matter, radiation energy is transformed into thermal energy. This phenomenon is responsible for heating by means of infrared radiation.

*** See Appendix III

netic resonance, mass spectrometry, etc.), infrared spectroscopy is a powerful tool in organic chemistry.

Although infrared radiation was discovered in 1800, the first spectroscopic studies in the infrared started a century later. This was primarily because of great technical difficulties and lack of a complete theoretical background. These difficulties were solved in the first four decades of our century.

Development of quantum theory and wave mechanics pointed out the great importance of infrared spectroscopy in the investigation of molecular structure.

The first hypothesis concerning the existence of a correlation between infrared spectra and chemical structure was proposed by Abney and Festings. They showed in 1881 that various functional groups give rise to certain absorption bands in the infrared spectrum, to the extent that the occurrence of these bands necessarily implies the existence of the respective functional groups in the molecule. All subsequent studies supported this hypothesis, not only in the infrared region close to the visible ($0.7 - 1.2\mu$) investigated by Abney and Festings, but also in the region of longer wavelengths.

The first assignment of a band was done by Julius in 1892, who correlated the absorption occurring at ca. 3000 cm^{-1} with the existence of a methyl group in the molecule. An outstanding achievement is due to W. W. Coblentz who, between 1905 - 1908, published a catalog of infrared absorption and emission spectra of numerous substances*.

Between 1919 - 1938 very few infrared spectrometers were in existence, and those were in research laboratories (mainly in physics). Subsequently the use of infrared spectroscopy increased dramatically. According to recent statistics several hundred infrared spectrometers were in use in 1947, over 3000 in 1958, and almost 5000 in 1960. It is very likely that currently more than 10,000 infrared spectrometers of various types are in use all over the world. Infrared spectroscopy is used most intensely in organic chemistry, both in fundamental and industrial research. Besides qualitative and quantitative analyses (identification, purity control) this method became very important in studies of molecular structure, chemical kinetics, and reaction mechanisms.

* The work was re-edited in 1962 by the Perkin-Elmer Corporation.

INTRODUCTION
TO THE THEORY OF INFRARED
SPECTRA

CHAPTER I

ELEMENTS OF QUANTUM THEORY

Infrared spectra arise from rotational and vibrational motions of the molecule. The theoretical background for the interpretation of these spectra is provided by classical and quantum mechanics. The elements of quantum theory and wave mechanics are outlined briefly in Chapter I.

1. Atomic Spectra; Bohr theory

a. **Stationary states. Quantum conditions.** The nuclear model of the atom supported by Rutherford's fundamental experiments on diffusion of α -particles does not obey the laws of classical electrodynamics. In such a model the electron should permanently emit electromagnetic radiations because of the acceleration it experiences in its motion in the Coulomb field of the nucleus. Progressively losing its energy, the electron should finally "collapse" into the nucleus. However, it is known that the atom is a stable system which emits radiations only under certain conditions. To explain the stability of the planetary model of the atom, Niels Bohr postulated the existence of *stationary electronic orbits*, characterized by discrete energy states known as *stationary states*. Stationary states are selected from the infinity of energy states possible in classical mechanics by means of certain *quantum conditions*; for example, from all *elliptical orbits* accessible to a single electron moving in the Coulomb field of a nucleus only those in which the major axis is proportional to the square of a whole number n , called the *principal quantum number*, are possible. The minor axis is proportional, with the same proportionality factor, to the product of n and a second number $l + 1$; l is the so-called *azimuthal quantum number*; n can take any integral value 1, 2, 3, . . . For a given value of n , l can take only the values 0, 1, 2, 3, . . . $n - 1$. Four quantum numbers are necessary to characterize a certain state of the electron. The other two quantum numbers, the so-called *magnetic quantum number* m_l and the *spin quantum number* m_s , are related to the orbital magnetic momentum and to the rotational momentum of the electron, respectively. According to Pauli's *exclusion principle*, no two electrons in an atom can have the same set of quantum numbers. The two sets must differ by at least one of the quantum numbers. It follows that in an orbit with a given n , l and m_l , there can be at the most two electrons that have opposite spin numbers.

b. **Frequency rule.** Contrary to classical electrodynamics, an atom does not emit electromagnetic radiations while the electron is moving in one of its allowed orbits. Emission takes place only if for some reason the electron loses energy in going from an initial orbit of energy E_i to another orbit of final energy E_f , lower than E_i . This phenomenon is called a *quantum jump*. The energy emitted as a *light quantum (photon)* corresponds to the difference in energy of the two states:

$$h\nu = E_i - E_f \quad (I-1)$$

The relation (I-1) is the second postulate in Bohr's theory and is called *frequency condition* or *frequency rule*. According to this postulate the frequency of the emitted radiation is given directly by the difference in energy between the final and initial states of the electron. The frequency rule holds for *absorption of radiations* as well. In this case the quantum jump (transition) takes place from a lower to an upper level ($E_f - E_i$). The system acquires energy and relation (I-1) has a positive value. Transitions cannot take place between any two levels. They are limited by *selection rules*, which state that only certain changes in quantum numbers, determining the level of the two states, are *allowed*. All other transitions are *forbidden*.

From (I-3) and (I-1) it follows that the wave number of the emitted or absorbed light is

$$\nu = \frac{E_i}{hc} - \frac{E_f}{hc} \quad (I-2)$$

The two terms E_i/hc and E_f/hc are called *spectral terms*. In molecular spectroscopy the expression *term* is often used instead of *energy state* or *quantum state* and the expression *term value* is synonymous with *energy value*. They differ only by the factor $1/hc$.

In the hydrogen atom or in the hydrogen-like ions He^+ , Li^{2+} , ... the possible values of the energy E_n for various stationary states of the electron are given by

$$E_n = - \frac{2\pi^2\mu e^4}{h^2} \cdot \frac{Z^2}{n^2}, \quad (I-3)$$

where n is the principal quantum number, μ the reduced mass of the electron and nucleus (see I-22) and Z (which is equal to 1 in the case of hydrogen) is the atomic number.

In the case of the motion of a single electron (sometimes called the optical electron)* about an atomic core which is no longer a point-like charge, the values of the energy are

$$E_{n,l} = \frac{2\pi^2\mu e^4}{h^2} \cdot \frac{Z^2}{(n + a)^2}, \quad (I-4)$$

* An optical electron is one with a principal quantum number larger than the quantum numbers of other electrons. Its linkage to the atom is sufficiently weak to be able to undergo a quantum jump.

where a is the Rydberg correction. This correction depends on the azimuthal quantum number l and goes rapidly to zero when l increases. In this case Z is the charge of the atomic core, (i.e. the difference between the atomic number of the corresponding element and the number of electrons in the atomic core). Consequently the energy values and the term values are functions of the quantum numbers. The wave number of the absorbed or emitted radiation can be expressed as a function of the quantum numbers (of the final and initial states). If we substitute different n or n and l values in (1-3) and (1-4), respectively, and calculate the corresponding term differences, we obtain the well-known series of lines (Lyman, Balmer, Paschen, Brackett, Pfund etc.) that represent spectra of various species of atoms or ionized atoms (hydrogen, lithium etc.).

c. *The correspondence principle.* Bohr's third postulate shows that for sufficiently large values of quantum numbers both the rules of quantum and classical theory are applicable. Transitions between energy levels with large quantum numbers do not change the energy state of the system to such an extent as to imply real discontinuity. Since quantum jumps are very small one may consider that in this region the processes are quasi-continuous. The correspondence principle enabled the old quantum theory to make use of many classical results, mainly, in intensity calculations.

2. Wave mechanics

The laws of classical (Newtonian) mechanics are applicable only to normal masses. Very small (submicroscopic) particles do not obey these laws. Since even Bohr's theory could not offer a satisfactory physico-mathematical treatment for the behavior of elementary particles, it became necessary to revise the bases of quantum theory and of the concepts regarding the nature of the particles.

In 1924 Louis de Broglie postulated that any corpuscle of matter can be associated with a wave. The wavelength is related to the momentum p of the particle by the expression:

$$\lambda = \frac{h}{p}, \quad (1-5)$$

where $p = mv$ (mass \times velocity).

This postulate, attributing to matter a dual character, that of particle and wave, is the fundamental principle of quantum mechanics (Heisenberg, 1925) and of wave mechanics (Schrödinger, 1926).

a. *The Schrödinger equation.* Wave mechanics does not describe a particle in motion by its position and velocity, but by a complex function of coordinates and time,

$$\Psi(x, y, z, t), \quad (1-6)$$

called the *wave function* of the particle. Since it contains the number i it has an irrational value. Only the square of its absolute value is rational and has a physical meaning. It represents the probability that a particle is present at time t in a point with coordinates x, y, z .

Thus the concept of Bohr's *orbit* is replaced by the concept of an *electron cloud* with a density proportional to the probability of the existence of the particle in a certain region. In the simple case of a sine motion one may write

$$\Psi = \psi \sin 2\pi\nu' t$$

or

$$\Psi = \psi \cos 2\pi\nu' t,$$

or combined

$$\Psi = \psi e^{-2\pi i\nu' t}, \quad (1-7)$$

where ψ is the amplitude of the motion.

For a single mass point of mass m with an amplitude depending solely on the coordinates x, y, z , Schrodinger wrote the equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0, \quad (1-8)$$

where the total energy of the particle $E = h\nu'$. The potential energy V is given by the same expression as in classical theory.

For a number of N particles the Schrodinger equation is

$$\sum_k \frac{1}{m_k} \left(\frac{\partial^2 \psi}{\partial x_k^2} + \frac{\partial^2 \psi}{\partial y_k^2} + \frac{\partial^2 \psi}{\partial z_k^2} \right) + \frac{8\pi^2}{h^2} (E - V) \psi = 0, \quad (1-9)$$

where the amplitude ψ depends on the $3N$ coordinates x_k, y_k, z_k ; m_k is the mass of the particle k .

Thus, in wave mechanics the motion of a particle is determined by a function $\psi(x, y, z)$, representing the solution of the Schrodinger equation. The solutions must be continuous, single-valued and finite and vanish at infinity.

An equation with linear partial derivatives like the Schrodinger equation satisfies the above conditions only for certain values of the constant E , called *eigenvalues*. Each value is related to an *eigenfunction*. When n eigenfunctions correspond to the same eigenvalue, we talk about an *n-fold degeneracy*.

The eigenvalues represent the energies of the particle in stationary states. Thus, Bohr's postulate acquires a mathematical meaning in wave mechanics.

b. **The interaction between radiation and matter.** The interaction of electromagnetic radiation with an atomic system is essentially an interaction with the electric dipole moment \vec{M} of the system*. The dipole moment is equal

* Interaction with the magnetic dipole moment, the quadrupole moment, etc., is also possible but with very low probabilities.

to the product of the electric charge e of the system and the vectorial distance \vec{r} between the centers of gravity of positive and negative charges:

$$\vec{M} = e \vec{r} \quad (\text{I-10})$$

with components

$$M_x = \sum e_k x_k, \quad M_y = \sum e_k y_k, \quad M_z = \sum e_k z_k, \quad (\text{I-11})$$

where e_k is the charge on the particle k and x_k , y_k , and z_k are the corresponding coordinates.

The interaction energy is $\vec{M} \cdot \vec{E}$, where \vec{E} is the electric vector of the wave. The effect of electromagnetic radiation on the motion of particles is primarily manifested by a change of the electric dipole moment with an accompanying change of the energy of the system. Since the value of the electric field (\vec{E}) is a periodic function, the variation of the dipole moment (\vec{M}) is also periodic (see Chapter II, Section 2b). Introducing the energy of interaction $\vec{M} \cdot \vec{E}$ into the wave equation, we find that the probability of transition between two states n and m due to this interaction (emission or absorption) is proportional to the square of vectors \vec{R}^{nm} called *transition moments* which are the matrix elements of the interacting dipole moment. If $\vec{R}^{nm} \neq 0$, the transition is *allowed*. If $\vec{R}^{nm} = 0$, the transition is *forbidden*.*

For instance, in the case of a system with a single electron, all \vec{R}^{nm} values are zero, except for those in which the quantum numbers l of states n and m differ by unity.

$$\Delta l = \pm 1 \quad (\text{I-12})$$

Thus we find the *selection rule* postulated by Bohr's theory.

The transition moments \vec{R}^{nm} depend on the eigenfunctions ψ_n and ψ_m of the states n and m . Hence the probability of the transition between these states is determined by the corresponding eigenfunctions. This now allows one to obtain the *intensity* of the resulting spectral line.

3. Molecular spectra

Unlike the atom the molecule is a more complex system. Its mass cannot be considered point-like. The mass of the molecule is practically concentrated in the atomic nuclei, which can be considered point-like. This gives the molecule a larger number of *degrees of freedom*. The molecule has *rotational moments of inertia*, nonexistent in the atom; on the other hand, *relative motions of the*

* If $n=m$, \vec{R}^{nn} is the permanent dipole (which is zero for the atom but can be different for a molecule).

atoms become possible in a molecule. Thus the molecule is characterized not only by its *electronic* and *translational energy* but also by its *rotational* and *vibrational energy*.

In a first approximation the total energy of a molecule can be considered as a sum of its electronic energy E_e , vibrational energy E_v , rotational energy E_r , and translational energy T :

$$E = E_e + E_v + E_r + T. \quad (1-13)$$

The translation has a continuous character (it cannot be quantized); this energy is not directly involved in emission or absorption of radiations. All the other forms of energy are quantized. In other words, the molecule can have only certain rotational, vibrational, or electronic states. Like the atom, the molecule can rise from a lower energy level to a higher energy level by absorbing a light quantum with an energy equal to the difference in energy between the two states.

The rotational energies of a molecule are small. Consequently, the energy difference between two *rotational levels* is also small and so is the energy (frequency) of the quanta necessary to accomplish the *transition* between these two levels. The corresponding quanta belong to the *micron* or *far infrared region* (above 30 μ). Vibrational energies are considerably higher; consequently, the energy difference between two *vibrational levels* is also higher. The quanta absorbed in a *vibrational transition* belong to the medium infrared region (ca. 3–30 μ) or to the *near infrared* (0.76–3 μ). The highest energies are required by *electronic transitions*. The corresponding quanta belong to the visible (0.1–0.76 μ) or ultraviolet* regions (below 0.1 μ).

Transitions in which higher energy levels are involved are accompanied by transitions involving lower levels; for instance, a transition between two vibrational states is always accompanied by rotational transitions, and electronic transitions are accompanied by both rotational and vibrational transitions. Consequently, a transition between two levels does not involve quanta of a single frequency but a series of quanta of different frequencies. Therefore vibrational spectra are much more complicated than pure rotation spectra; in fact, their correct name is *rotation-vibration spectra*. Obviously, *electronic spectra* are the most complicated.

Whereas *atomic emission spectra* (in the ultraviolet or visible region) consist of *lines* with initially large separations rapidly converging to the so-called band head in rotation-vibration spectra of gases, the almost equidistant "lines" are crowded into a very narrow spectral region forming a *fine structure band*. In many instances only the *envelope* of this band can be recorded.

In spectra of molecules in the liquid or solid state, bands varying in width from narrow to broad are observed, revealing the complexity of the

* In some very rare cases (e.g., some cyanine dyes) electronic transitions can occur also in the near infrared.

transitions. The *position*, *shape*, and *intensity* of these bands are the most important characteristics used in the spectroscopic studies of organic molecules.

In a first approximation each of the three forms of energy mentioned above can be treated separately, considering the other two as being constant. Actually, this is possible only in the case of rotation because the energy required for pure rotational transitions does not affect the vibrational and electronic states. In the case of vibrational and electronic transitions the procedure is used only to simplify the theoretical treatment. The approximation is satisfactory in the case of diatomic molecules. It is also applied to polyatomic molecules although in this case mutual interactions of the three types of motions result in a much more complicated pattern.

CHAPTER 2

INFRARED SPECTRA OF DIATOMIC MOLECULES

Diatomic molecules are the simplest possible systems for theoretical studies of rotational and vibrational motions.

They offer the possibility of comparing theoretical predictions with experimental results. For this reason diatomic molecules are usually treated separately in the theory of molecular spectroscopy. Accordingly, this approach is used here.

Chapter 2 deals with rotation and vibration of diatomic molecules, using the rigid rotator, the non-rigid rotator, the harmonic oscillator, and the anharmonic oscillator as models. It also deals with interactions of rotation and vibration and with rotation-vibration spectra of diatomic molecules. The actual examples are molecules in the gaseous state at a sufficiently low pressure so that rotations and vibrations are considered to be free of external influences (due to the proximity of other molecules).

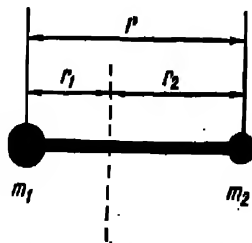


Fig. I-3 The rigid rotator.

1. Rotation of diatomic molecules

a. **The rigid rotator.** The simplest model of a diatomic molecule is that of a dumbbell with two point-like atoms of masses m_1 and m_2 rigidly bound to each other by a massless axis (Fig. I-3). Such a system can rotate about three mutually perpendicular axes that have their origin in the center

of gravity of the masses m_1 and m_2 . The moment of inertia about the inter-nuclear axis is practically zero* and the corresponding rotation does not manifest itself in any way. The moments of inertia about the other two axes being equal, it is sufficient to consider only the rotation about one of them.

The energy of rotation, equal to the kinetic energy of the system, is

$$E_{\text{rot}} = \frac{m_1 v_1^2}{2} + \frac{m_2 v_2^2}{2}, \quad (\text{I-14})$$

where velocities v_1 and v_2 are determined by the radii of rotation and the angular velocity ω :

$$v_1 = r_1 \omega, \quad v_2 = r_2 \omega. \quad (\text{I-15})$$

Substitution of v_1 and v_2 in (I-14) gives

$$E_{\text{rot}} = \frac{1}{2} \omega^2 (m_1 r_1^2 + m_2 r_2^2). \quad (\text{I-16})$$

The sum in brackets is the moment of inertia I about the axis of rotation:

$$I = \sum m_i r_i^2. \quad (\text{I-17})$$

It follows that

$$E_{\text{rot}} = \frac{1}{2} I \omega^2. \quad (\text{I-18})$$

Since

$$r_1 = \frac{m_2}{m_1 + m_2} r, \quad r_2 = \frac{m_1}{m_1 + m_2} r, \quad \text{and} \quad r_1 + r_2 = r, \quad (\text{I-19})$$

the moment of inertia may be expressed by

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 \quad (\text{I-20})$$

or

$$I = \mu r^2, \quad (\text{I-21})$$

where μ is the reduced mass of the system m_1 and m_2 :

$$\mu = \frac{m_1 m_2}{m_1 + m_2}. \quad (\text{I-22})$$

This means that the rotation of a system of two mass points of masses m_1 and m_2 (Fig. 1-4a) may be described by the rotation of an equivalent and simpler system consisting of a single mass point of mass μ at the distance r from the axis (Fig. 1-4b).

This system is called the *simple rigid rotator*.

* The diameter of the nuclei being extremely small, the distance between the masses and the corresponding axes of rotation may be considered to be nearly zero.

b **Energy levels and spectrum of the simple rigid rotator.** For a simple rigid rotator the Schrödinger equation is*

$$\frac{\partial^2 \psi}{\partial \tau^2} + \frac{\partial^2 \psi}{\partial \theta^2} + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 \mu}{h^2} E \psi = 0 \quad (1-23)$$



Fig. 1-1 Rotation of a rigid system
(a) System of two mass points, (b) Simple rigid rotator

The eigenvalues of this equation** are given by

$$J_{rot} = \frac{h^2 J(J+1)}{8\pi^2 \mu} = \frac{h^2}{8\pi^2 I} J(J+1) \quad (1-24)$$

where J , the rotational quantum number, can take the integral values 0, 1, 2, ... Equation (1-24) gives a series of discrete energy levels. The energy of each level is proportional to J^2 (Fig. 1-5a)

According to (1-2) the wave number of a radiation absorbed during a rotational transition is given by the difference between the terms corresponding to the levels associated with the quantum jump.

Considering the energy value (1-24), the *rotational term* is given by

$$F(J) = \frac{E_{rot}}{hc} = \frac{h}{8\pi^2 c I} J(J+1). \quad (1-25)$$

Letting

$$\frac{h}{8\pi^2 c I} = B \quad (1-26)$$

equation 1-25 becomes

$$F(J) = BJ(J+1). \quad (1-25a)$$

B is called the *rotational constant*. Its value is $(27.986/I) 10^{-40} [\text{cm}^{-1}]$.

The selection rule for rotation shows that only transitions in which the quantum number changes by one unit are allowed

$$\Delta J = \pm 1. \quad (1-27)$$

* Refer to equation 1-8, where m is replaced by μ (the reduced mass), $V=0$ (because the potential energy of the rigid rotator is zero), and $r^2 = \theta^2 + \phi^2 = r^2$ (a constant)

** The solution of the Schrödinger equation can be found in Ref. 11-14

Consequently the value of rotational terms can be expressed as a function of a single quantum number J assigned to the initial state. In this case the wave number of the absorbed radiation is

$$\begin{aligned} \nu &= F(J+1) - F(J) \\ &= B(J+1)(J+2) - BJ(J+1) \quad (1-28) \\ &= 2B(J+1), \end{aligned}$$

where $J=0, 1, 2, 3, \dots$

Equation 1-28 shows that the spectrum of the simple rigid rotator consists of a number of lines separated by a constant difference $2B$. The first line lies at $\nu = 2B$ (Fig. 1-5b) and corresponds to the transition from zero rotational energy to the first allowed rotational state.

c. **The nonrigid rotator.** The rigid rotator cannot be considered a perfect model for a diatomic molecule rotating about the center of gravity. In reality, as a result of the action of the centrifugal force, the internuclear distance varies with the velocity of rotation. This suggests the replacement of the rigid bar by a weightless spring resulting in a new model, the *nonrigid rotator*.

d. Energy levels and spectrum of the nonrigid rotator.

In a nonrigid rotator both the internuclear distance and the moment of inertia are causally altered by the centrifugal force. This results in a variation of B (1-26) which is no longer constant.

The term of the nonrigid rotator is given with sufficient accuracy by:

$$F(J) = \frac{E_{\text{rot}}}{hc} = B[1 - uJ(J+1)]J(J+1) \quad (1-29)$$

where $B[1 - uJ(J+1)]$ replaces B in (1-25). The constant B is given by (1-26) in which I has a value corresponding to zero rotational energy; the value of u is much smaller than unity.

Letting

$$uB = D_{cf}, \quad (1-30)$$

the rotational term of the nonrigid rotator is given by

$$F(J) = BJ(J+1) - D_{cf}J^2(J+1)^2. \quad (1-31)$$

If J is not very large the influence of the centrifugal factor D_{cf} is very small. In Fig. 1-6 energy levels of the nonrigid rotator (solid line) obtained for exaggerated values of D_{cf} are compared with energy levels of the rigid rotator (dotted line). Even in this case, for $J < 6$ the influence of the centrifugal factor D_{cf} is so small that it cannot be shown in the diagram.

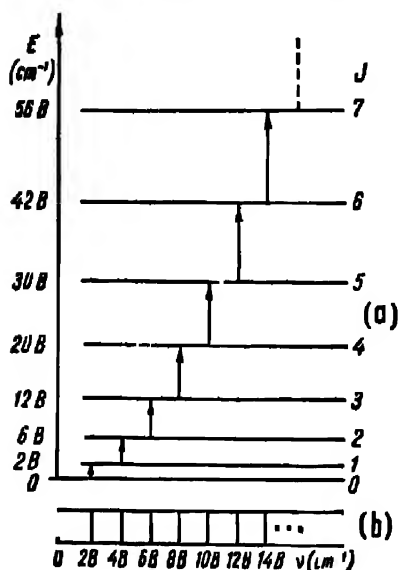


Fig. 1-5 (a) Energy levels and transitions of a rigid rotator and (b) the corresponding infrared spectrum.

The selection rule $\Delta J = \pm 1$ is applicable to the nonrigid rotator as well. Consequently the wave number of the radiations absorbed by the nonrigid rotator is given by the difference between neighboring terms.

$$\begin{aligned} \nu &= F(J+1) - F(J) \\ &= B(J+1)(J+2) - D_{cf}(J+1)^2(J+2)^2 - BJ(J+1) + D_{cf}J^2(J+1)^2 \\ &= 2B(J+1) - 12D_{cf}(J+1)^3 \end{aligned} \quad (I-32)$$

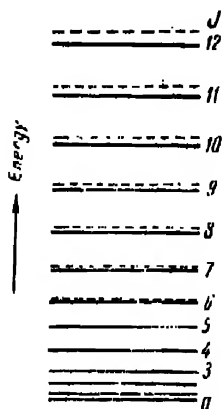


Fig. I-6 Energy levels of the nonrigid rotator (From Herzberg [1a]).

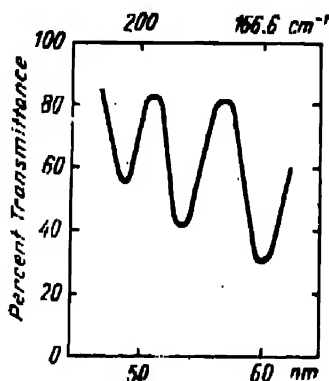


Fig. I-7 Rotation spectrum of hydrogen chloride [1a].

Thus in the *infrared rotation spectrum* lines are not equidistant; the distance decreases with increasing rotational quantum number. However since D_{cf} is much smaller than B ($D_{cf} < 10^{-4} B$), the effect is very small. The agreement between calculated and experimental values shows that the model of the nonrigid rotator is very suitable for explaining far infrared spectra. From the observed spectra important data can be obtained. B (see Section 1b of this chapter) allows us to calculate the moment of inertia I (I-26) and the internuclear distance (I-21). The rotational constant D_{cf} gives a measure of the influence of the centrifugal force and may be used to determine the approximate vibrational frequency of the molecule (See Section 2d of this chapter).

The following data have been obtained from the rotation spectrum of hydrogen chloride (Fig. I-7 and Table I-1):

$$B = 10.34 \text{ cm}^{-1} \text{ (distance between two lines, } 2B = 20.68 \text{ cm}^{-1})$$

$$D_{cf} = 0.0004 \text{ cm}^{-1}$$

$$I = 2.71 \cdot 10^{-40} \text{ g. cm}^2$$

$$r = 1.29 \cdot 10^{-8} \text{ cm } (\mu = 1.63 \cdot 10^{-24} \text{ g}).$$

The experimental results have lead to a number of empirical equations. The simplest,

$$\nu = f_0 m, \quad (I-28a)$$

Table I-1 Rotational frequencies of the HCl molecule (from Herzberg [1a])

| $m = J + 1 - J$ (initial) | ν_{calc} (I-28a) ($f_0 = 20.68$) | ν_{obs} cm^{-1} | $\Delta\nu_{\text{obs}}$ cm^{-1} | ν_{calc} (I-32 a) ($f_0 = 20.79$) ($q = 0.0016 \text{ cm}^{-1}$) | $\nu_{\text{obs}} - \nu_{\text{calc}}$ (I-32 a) |
|---------------------------|---|--|--|---|--|
| 1 | 0 | 20.68 | | 20.79 | |
| 2 | 1 | 41.36 | | 41.57 | |
| 3 | 2 | 62.04 | | 62.33 | |
| 4 | 3 | 82.72 | 83.03 | 83.06 | -0.03 |
| | | | 21.1 | | |
| 5 | 4 | 103.40 | 104.1* | 103.75 | +0.35 |
| | | | 20.2 | | |
| 6 | 5 | 124.08 | 124.30 | 124.39 | -0.09 |
| | | | 20.73 | | |
| 7 | 6 | 144.76 | 145.03 | 144.98 | +0.05 |
| | | | 20.48 | | |
| 8 | 7 | 165.44 | 165.51 | 165.50 | +0.01 |
| | | | 20.35 | | |
| 9 | 8 | 186.12 | 185.86 | 185.91 | 0.08 |
| | | | 20.52 | | |
| 10 | 9 | 206.80 | 206.38 | 206.30 | +0.06 |
| | | | 20.12 | | |
| 11 | 10 | 227.48 | 226.50 | 226.55 | 0.05 |

is comparable to (I-28), $2B$ corresponds to f_0 (a characteristic constant of the gas), and $(J + 1)$ corresponds to the integral number m . The differences between calculated and observed frequencies are even smaller if one adds a cubic term to Equation (I-28a). In this case one obtains an expression comparable to (I-32):

$$\nu = f_0 m - g m^3 \quad (\text{I-32a})$$

where the factor g is much smaller than f_0 (see Table I-1). The values of r and I are in agreement with those obtained by other physical methods (viscosity measurements and crystallography).

As previously mentioned the activity of pure rotational (and vibrational) modes in the infrared is determined by the variation of the dipole moment. Obviously, in the case of diatomic molecules this condition holds only for heteroatomic molecules with a permanent dipole. Homopolar diatomic molecules (H_2 , O_2 , N_2 , etc.) do not absorb in the infrared**.

* This value has not been accurately measured.

** Recent experiments have shown that perturbation of the symmetry of these molecules under the influence of strong external fields results in the so-called *induced absorption*, independent of changes in dipole moment but dependent on the product of the polarizability of the molecule and field intensity. This product is called the *induced momentum*. Since the phenomenon depends on the polarizability of the molecule, the induced absorption obeys the selection rules valid in the Raman effect. Induced absorption spectra of hydrogen, oxygen, and nitrogen have been obtained both in the gaseous state at high pressure and in the condensed phase. In both cases intermolecular collisions give rise to sufficiently strong fields ($\text{ca. } 10^6 \text{ V/cm}$) for induced absorption to occur.

2. Vibration of diatomic molecules

For studies of vibrational motions of diatomic molecules the same previously described dumbbell model is used. The atoms are connected by a massless spring and only vibrations taking place under the influence of the force of the spring are considered. These motions occur periodically about an equilibrium position in the direction of the internuclear axis.

a **The harmonic oscillator.** As in the case of the rigid rotator the system (Fig. I-8a) can be reduced to a mass point periodically oscillating about an equilibrium position (Fig. I-8b). If the force that tends to bring the mass point to its equilibrium position is proportional to the elongation x ,

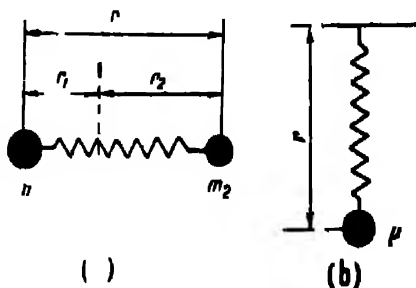


Fig. I-8 The harmonic oscillator

$$F = -kx \quad (I-33)$$

the system is called a *harmonic oscillator* and k is the *force constant*.

Equation (I-33) may be written as a differential equation by replacing the force F by the product *mass \times acceleration*

$$m \frac{d^2x}{dt^2} = -kx \quad (I-34)$$

The solution of this equation is

$$x = x_0 \sin(2\pi\nu_v' t) \quad (I-35)$$

where x_0 is the amplitude of the vibration. The vibrational frequency ν_v' is given by

$$\nu_v' = \frac{1}{2\pi} \left(\frac{k}{m} \right)^{1/2} \quad (I-36)$$

The potential energy of the harmonic oscillator is obtained by integrating the expression (I-33)

$$V = \frac{1}{2} kx^2 = 2\pi^2 m \nu_v'^2 x^2 \quad (I-37)$$

Since the potential energy of the harmonic oscillator is a second order function of x it is represented by a parabola with the concavity toward positive values of the energy axis. Its apex (the minimum potential energy) corresponds to the equilibrium position r_0 (Fig. I-9).

In the case of two atoms of a molecule the mutually restoring forces acting when the atoms are displaced from their equilibrium position r_0 may be considered to be proportional to the change of the interatomic distance

$$m_1 \frac{d^2 r_1}{dt^2} = -k(r - r_0) \quad (I-38a)$$

and

$$m_2 \frac{d^2 r_2}{dt^2} = -k(r - r_e). \quad (\text{I-38b})$$

The definitions of r_1 , r_2 and r are given in Fig. I-8 (see also Fig. I-3). In Fig. I-8, $r = r_e$ (see also Fig. I-9). From (I-38a) and (I-38b), we obtain the equation of the harmonic oscillator by substitution of (I-19) and (I-22), reducing the vibration of the two atoms of a molecule to the vibration of a single mass point of mass μ :

$$\frac{d^2(r - r_e)}{dt^2} = -k(r - r_e). \quad (\text{I-38})$$

The vibrational frequency of the molecule is

$$\frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} \quad (\text{I-39})$$

Thus, the rules of classical mechanics state that in a diatomic molecule there is only one possible vibrational frequency. This frequency depends on the force constant and on the reduced mass of the two atoms. It is independent of the amplitude, provided that (I-33) is obeyed. Determination of the force constant is one of the major goals in spectroscopic research since the force constant gives quantitative information concerning the interatomic forces.

b. **Energy levels and spectrum of the harmonic oscillator.** In classical mechanics the amplitude (therefore the vibrational energy) can take *any* value. In wave mechanics the Schrödinger equation describing the motion of the linear harmonic oscillator is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2} \left(E - \frac{1}{2} k x^2 \right) \psi = 0. \quad (\text{I-40})$$

The eigenvalues obtained from this equation are given by

$$E(v) = \frac{h}{2\pi} \left[\frac{k}{\mu} \left(v + \frac{1}{2} \right) \right] = h\nu_v \left(v + \frac{1}{2} \right), \quad (\text{I-41})$$

where v , the *vibrational quantum number*, can take only integral values 0, 1, 2, ... Consequently, the harmonic oscillator can have only *certain* energy levels depending on the quantum number v . The difference in energy between two levels is constant. Therefore, in Fig. I-9, the energy levels of the harmonic oscillator are equidistant.

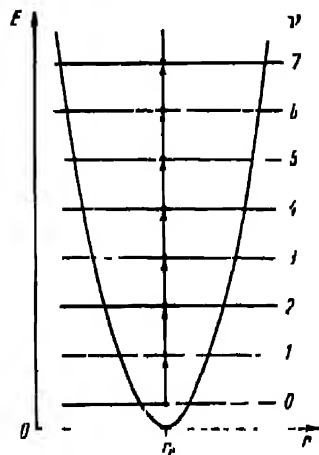


Fig. I-9 The potential energy curve, energy levels and transitions of the harmonic oscillator

Even at the lowest level ($v=0$), the energy is not zero (in contrast to the rotator), but $E(0)=1/2 (h\nu_0)$. This energy is called *zero point energy*. Sometimes the quantum state $v=0$ is improperly called the *vibrationless state*.

Dividing the energy by hc , one obtains the value of the *vibrational term of the harmonic oscillator*:

$$G(v) = \frac{E(v)}{hc} = \frac{\nu_0}{c} \left(v + \frac{1}{2} \right) \quad (1-42)$$

Letting

$$\frac{\nu_0}{c} = \omega, \quad (1-43)$$

one obtains

$$G(v) = \omega \left(v + \frac{1}{2} \right) \quad (1-44)$$

where ω is the wave number. It corresponds to the frequency in (1-36) given by classical mechanics.

The selection rule for the vibrational quantum number of the harmonic oscillator is

$$\Delta v = \pm 1. \quad (1-45)$$

The term difference gives the wave number of the absorbed radiation:

$$\nu = G(v+1) - G(v) = \omega \left(v + \frac{3}{2} \right) - \omega \left(v + \frac{1}{2} \right) = \omega. \quad (1-46)$$

This shows that the interaction between radiation and matter takes place when the frequency of the radiation is equal to the frequency of the molecular vibration. In other words the dipole moment must change with a frequency equal to the frequency of the changing electric field \vec{E} . Absorption of energy results in an increase in amplitude of the molecular vibration. The absorbed quanta remain the same no matter what levels are involved in the transition (Fig. 1-9).

Thus the vibrational spectrum of a diatomic molecule considered as a harmonic oscillator has a single strong band in the near or medium infrared in contrast to the rotational spectrum consisting of several almost equidistant lines.

c. **The anharmonic oscillator.** The model of an harmonic oscillator does not represent exactly the behavior of an actual molecule. In such a model the potential energy increases indefinitely with increasing internuclear distance (Fig. 1-10, curve 1). Experiment shows that when the internuclear distance becomes very large the attractive force is zero and the potential energy becomes constant. This behavior is shown in curve 2, Fig. 1-10.

On the other hand, infrared spectra of diatomic molecules show, along with strong bands corresponding to the transition $\Delta v=1-0$ (called *fundamental*), a number of additional bands (called *overtones*). The frequency of the overtones is two, three, four,...

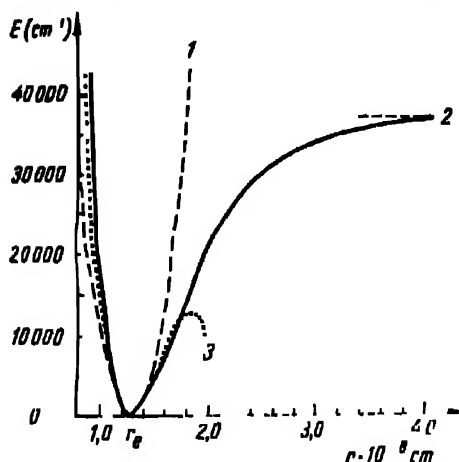


Fig. I-10 Potential energy curve of an anharmonic oscillator [1a].

times larger than the fundamental frequency. They arise from transitions where $\Delta v=2, 3, 4, \dots$. Although their intensity is much lower than that of the fundamental, the first overtones have been detected experimentally by progressively increasing the gas-cell length to several meters at normal pressure. Figure I-11 is a schematic spectrum of hydrogen chloride. It can be seen that the intensity of the overtones is much smaller than that of the fundamental. The distance between bands is not rigorously constant; it decreases slightly with increasing frequency. This confirms the anharmonicity of molecular vibrations.

For the actual, potential-energy curve 2 in Fig. I-10, there is no rigorous mathematical expression. In order to obtain a better approximation one has to add a cubic or higher terms to the parabolic function of the harmonic oscillator.

$$V = f(r - r_e)^2 - g(r - r_e)^3. \quad (I-17)$$

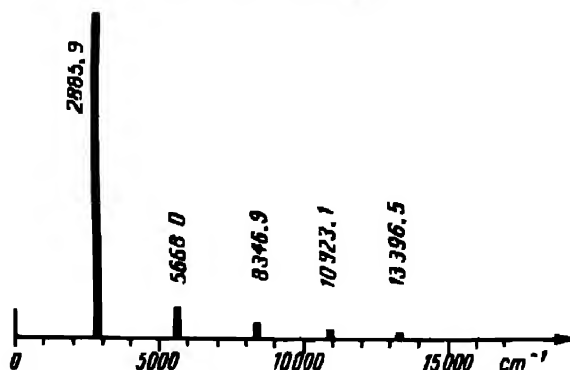


Fig. I-11 Schematic spectrum of hydrogen chloride. In reality intensities decrease much faster.

Equation (I-17) (where $g \ll f$) gives curve 3 in Fig. I-10. In recent years, elaborate computer work resulted in very good approximations for the potential energy of some diatomic molecules.

Although remaining strictly periodic, the motion of the anharmonic oscillator does not have a pure sine form. Classically it can be represented as a superimposition of fundamental and overtone vibrations (Fourier series)

$$x = x_{01} \sin 2\pi\nu_1 t + x_{02} \{1 + \cos 2\pi 2\nu_2 t\} + x_{03} \sin 2\pi 3\nu_3 t \quad (1-18)$$

where x_{01} , x_{02} , x_{03} are the amplitudes of the fundamental and of the overtones. The smaller the anharmonicity ($q \ll f$) the smaller the amplitudes of the overtones ($x_{02} \ll x_{01}$, and $x_{03} \ll x_{02}$). However, the importance of the overtones increases with increasing amplitude of the fundamental x_{01} (since x_{02} and x_{03} are proportional to the square and cube respectively of x_{01}).

Only for small amplitudes is the frequency of the vibrations given by (1-34). It decreases as the amplitude x_{01} increases.

d **Energy levels and spectrum of the anharmonic oscillator.** The eigenvalues obtained from the Schrödinger equation by substituting (1-17) as potential energy are given by

$$E(v) = h\nu \left(v + \frac{1}{2}\right) - h\nu x_e \left(v + \frac{1}{2}\right)^2 + h\nu y_e \left(v + \frac{1}{2}\right)^3 + \quad (1-19)$$

The vibrational terms are

$$G(v) = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \omega_e y_e \left(v + \frac{1}{2}\right)^3 + \quad (1-20)$$

The constant $\omega_e x_e \ll \omega_e$ and $\omega_e y_e \ll \omega_e x_e$. These constants are referred to infinitesimal amplitudes about the equilibrium position (r). Since q is nearly always positive, $\omega_e x_e$ is always positive, $\omega_e y_e$ can be positive or negative but it is almost always negligible. According to the term (1-20) in an anharmonic oscillator the separation between energy levels decreases slowly with increasing vibrational quantum number v (fig. 1-12a). The zero point energy ($v=0$) is

$$G(0) = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e + \frac{1}{8} \omega_e y_e \quad (1-21)$$

Adopting international notations

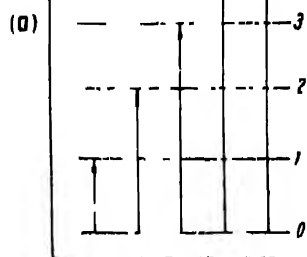
$$\begin{aligned} \omega_0 &= \omega_e - \omega_e x_e + \frac{1}{4} \omega_e y_e \\ G_0(v) &= G(v) - G(0) = \omega_0 v - \frac{1}{2} \omega_e y_e v^2 \\ \epsilon_0(v) &= \epsilon(v) - \epsilon(0) \end{aligned} \quad (1-22)$$

and referring the energy levels of the anharmonic oscillator to the zero point energy (not to the actual zero energy) one can write

$$\epsilon_0(v) = G(v) - G(0) = \omega_0 v - \frac{1}{2} \omega_e y_e v^2 \quad (1-23)$$

The selection rule of the anharmonic oscillator predicts, along with transitions where $\Delta v = \pm 1$ (the only ones allowed in the case of the harmonic oscillator), transitions where $\Delta v = \pm 2, \pm 3, \dots$ (Fig. I-12a). If all the molecules are in the fundamental state ($v=0$), all absorptions corresponding to

quantum jumps $\Delta v = 1, 2, \dots$ are possible. In this case the bands are characterized by the quantum numbers of the final and initial states; for example, the band 1-0 is referred to as fundamental, the band 2-0 as first overtone, etc. Given the anharmonicity, the frequencies of the bands 2-0, 3-0, ... are not exactly two, three, ... times the frequency of the 1-0 band, but the differences are very small.



If v' is the quantum number of the final state, term differences give wave numbers of the absorption bands occurring in the spectrum of an anharmonic oscillator (Fig. I-12b).

$$\nu = G(v') - G(0) = G_0(v') \quad (I-54)$$

(b)

Fig. I-12 Energy levels of the anharmonic oscillator.

Thus the frequency of the absorption bands gives directly the positions of the energy levels above the lowest energy level ($v=0$) (compare I-51 with I-53). If the cubic term in (I-51)

is neglected, the separation of two successive absorption bands is equal to the separation of the corresponding energy levels,

$$\begin{aligned} \Delta G_{v+1/2} &= G(v+1) - G(v) = G_0(v+1) - G_0(v) \\ &= \omega_e - 2\omega_e x_e v - 2\omega_e x_e v^2 = \omega_0 - \omega_0 x_0 - 2\omega_0 x_0 v. \end{aligned} \quad (I-55)$$

Subtracting further neighboring values obtained in (I-55), one obtains a constant value

$$\Delta^2 G_{v+1/2} = \Delta G_{v+1/2} - \Delta G_{v-1/2} = -2\omega_e x_e = -2\omega_0 x_0. \quad (I-56)$$

The constants $\omega_e x_e$ and $\omega_0 x_0$ in (I-56) are a measure of the anharmonicity of the motion. The increase in anharmonicity parallels the increase of the difference in (I-56.) The values of the vibrational constants ω_e and ω_0 are then obtained from (I-54) and (I-55) if one knows the frequency of one band, for example the strongest (1-0) band.

$$\nu(1-0) = G(1) - G(0) = G_0(1) = \omega_e - 2\omega_e x_e = \omega_0 - \omega_0 x_0. \quad (I-57)$$

Better results are obtained if all observed bands are used and the most appropriate values selected. Experimental data obtained for some diatomic molecules agree fully with the theoretical values.

The vibrational frequency ω may be also determined by using the rotational constants B and D_{cf} . The smaller the ω , the larger the potential energy curve (I-37). This means that r increases more rapidly under the stronger influence of the centrifugal force. Consequently, the rotational constant D_{cf} is larger for smaller values of ω . If the vibration is considered harmonic, the mathematical relation between the three constants is

$$D_{cf} = 4B^3$$

The value thus obtained for ω is obviously much less accurate, since the vibrational frequency is much larger than B , which in turn is much larger than D_{cf} .

3. Vibration-rotation motion of diatomic molecules

a. **The vibrating rotator.** After having described separately the rotational and vibrational motion of a diatomic molecule, one must consider the actual case where both types of motion take place simultaneously. The corresponding mechanical model is the *vibrating rotator*, which could also be called the *rotating oscillator*.

b. **Energy levels and spectrum of the vibrating rotator.** The permanently changing internuclear distance during the motion of the vibrating rotator implies a corresponding change of the moment of inertia and thus of the rotational constant B . A mean value of the rotational constant B_v has to be used in the vibrational state considered.

$$B_v = \frac{h}{8\pi^2 c \mu} \left[\frac{1}{r^2} \right], \quad (\text{I-61})$$

where $\left[\frac{1}{r^2} \right]$ is the mean value of the ratio $1/r^2$. Since the effect of the anharmonic vibration is an increase in the mean internuclear distance, the values of the B_v is smaller than in the case of the equilibrium distance (I-26). The value of B_v is given by

$$B_v = B_0 - \sigma_v \left(v + \frac{1}{2} \right) + \dots \quad (\text{I-62})$$

where $\sigma_v \ll B_0$. Similarly, the rotational constant D_{cf} is given by

$$D_v = D_0 + \beta_v \left(v + \frac{1}{2} \right) + \dots \quad (\text{I-63})$$

where $\beta_v \ll D_0$.

Introducing the values of the constants B_v and D_v into (I-31), one obtains for the *rotational term in a given vibrational state*,

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2 + \dots \quad (\text{I-64})$$

In this case the term T of the vibrating rotator is

$$T = G(v) + F_v(J) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \dots \quad (I-65)$$

$$+ B_v J(J+1) - D_v J^2(J+1)^2 + \dots$$

The energy levels of the vibrating rotator are given in Fig. I-13.

The selection rules for rotational and vibrational transitions are applicable to the vibrating rotator. Also, $\Delta v = 0$ is now allowed. If v' and J' are quantum

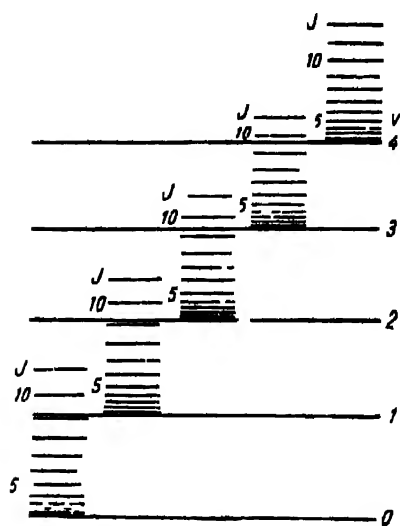
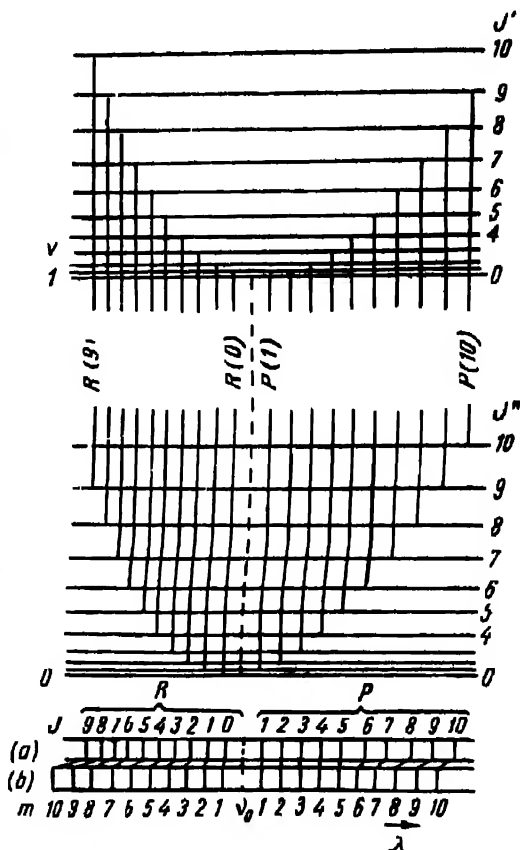


Fig. I-13 Energy levels of the vibrating rotator [1a]

Fig. I-14 Fine structure of a rotation band. The separation of vibrational levels is much larger compared to the separation of rotational levels shown in the figure.

(a) and (b) show schematic spectra with and without allowance for the interaction between vibration and rotation [1a]



numbers of the final state and v'' and J'' quantum numbers of the initial state, we obtain for the wave numbers of the lines of a rotation-vibration band

$$\nu = T' - T'' = G(v') + F_v(J') - G(v'') - F_v(J''). \quad (I-66)$$

For the pure vibrational transition ($J' = J'' = 0$) the vibration frequency $\nu_0 = G(v') - G(v'')$. Since the constant D_v is very small, the corresponding terms can be neglected. Relation (I-66) can be written

$$\nu = \nu_0 + B'_v J'(J'+1) - B''_v J''(J''+1). \quad (I-66a)$$

Taking into account that $\Delta J = \pm 1$, we can consider transitions with respect to a single quantum number J . For $\Delta J = +1$ we obtain

$$\nu_R = \nu_0 + 2B'_v + (3B'_v - B''_v)J + (B'_v - B''_v)J^2; J=0,1,\dots, \quad (I-67)$$

and for $\Delta J = -1$,

$$\nu_P = \nu_0 - (B'_v + B''_v)J + (B'_v - B''_v)J^2; J=1,2,\dots \quad (I-68)$$

Therefore, the rotation-vibration band consists of two series of lines called *R* and *P* branches, respectively. Both in the lower and the higher vibrational levels, the smallest value of J is zero. Consequently in the *R* branch, the smallest value of J'' is zero, and in the *P* branch it is 1 (Fig. I-14).

If one considers $B'_v = B''_v = B$ (neglecting the interaction of rotation and vibration), relations (I-67) and (I-68) can be written:

$$\nu_R = \nu_0 + 2B + 2BJ, \quad J=0,1,\dots, \quad (I-69)$$

$$\nu_P = \nu_0 - 2BJ, \quad J=1,2,\dots \quad (I-70)$$

which shows that the rotation-vibration band is formed of two series of equidistant lines: the first one goes from ν_0 toward larger wave numbers forming branch *R* and the second, toward smaller wave numbers forming branch *P*. The spectrum corresponding to equations (I-69) and (I-70), shown in Fig. I-14, is in very good agreement with the experimental spectrum. The interaction rotation-vibration ($B'_v \neq B''_v$) results in a slight convergence of lines. If $B''_v < B'_v$, the spacing of lines in the *R* branch decreases with increasing frequency. In the *P* branch the spacing increases (Fig. I-14a). The two branches of the band can be expressed by a single equation

$$\nu = \nu_0 + (B'_v + B''_v)m + (B'_v - B''_v)m^2, \quad (I-71)$$

where m is the running number of the lines. For the *R* branch, $m = J + 1$, and for the *P* branch, $m = -J$. In other words, the rotation-vibration band can be represented by a single series of lines for which the line corresponding to $m=0$ is missing. This line is called the *zero line* or *band origin*. It does not occur since a transition between two vibrational levels not accompanied by a change in rotational level ($\Delta J=0$) is forbidden.

Equation I-71 is perfectly similar to the empirical formula*

$$\nu = c + d m + e m^2 \quad (I-72)$$

where c , d and e are constants and m is the same as in (I-71). The rotational constants B'_v and B''_v can be determined directly from

$$d = B'_v + B''_v, \quad (I-73)$$

$$e = B'_v - B''_v,$$

derived from (I-71) and (I-72). In the vicinity of the frequency ν_0 , the difference between B'_v and B''_v is very small and (I-69) and (I-70) are in good agreement with the observed spectra. Consequently, the separation of two successive lines in this region is ca. $2B$. The convergence of lines increases with increasing difference $B'_v - B''_v$, i.e. with increasing Δv . In other words, the convergence is more accentuated for higher overtones.

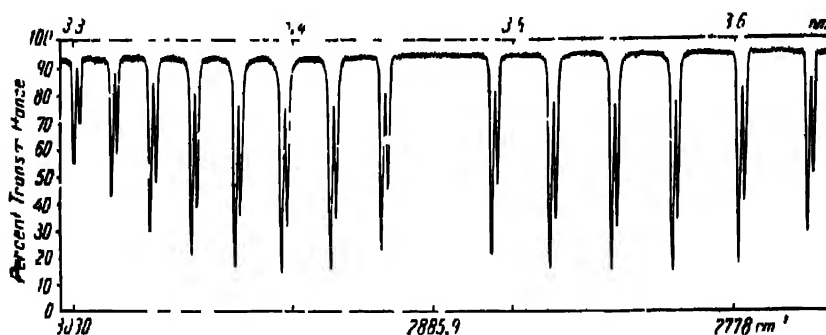


Fig. 1-14 Infrared spectrum of hydrogen chloride

The rotational constants can be also determined using the separation of the successive lines, $\Delta\nu(m)$, and the increase of this separation, $\Delta^2\nu(m)$. According to (I-71), the separation of two successive lines ($m+1$) and m is

$$\Delta\nu(m) = \nu(m+1) - \nu(m) = 2B'_v + 2(B'_v - B''_v)m, \quad (\text{I-71})$$

and the increase of the separation is

$$\Delta^2\nu(m) = \Delta\nu(m+1) - \Delta\nu(m) = 2(B'_v - B''_v) \quad (\text{I-75})$$

The second difference is constant. Its mean value gives satisfactory values for $2(B'_v - B''_v)$.

The infrared spectrum of hydrogen chloride (Fig. I-15), recorded with a high resolution spectrometer, is in complete agreement with the theoretical data. Table I-3 shows the observed frequencies, the separation of successive lines $\Delta\nu(m)$, and the values $\Delta^2\nu(m)$.

c. **The symmetric top.** In order to find a still better model for the study of infrared spectra of diatomic molecules, we finally have to consider the rotation about the internuclear axis (the figure axis). In all previous examples we neglected the moment of inertia resulting from the revolution of electrons about the nuclei. Since the mass of the electron is extremely small, this moment is very small, but it is not exactly zero.

The new model (Fig. I-16) in which two of the three moments of inertia are equal is called the symmetric top. In contrast to the moments of inertia, the corresponding angular momenta are of the same order of magnitude since

Table I-3 Fine structure of the absorption band of H^{35}Cl at 2890 cm^{-1}

| m | $\nu_{\text{obs}}(m)$ cm^{-1} | $\Delta\nu(m)$ cm^{-1} | $\Delta^2\nu(m)$ cm^{-1} | $\nu_{\text{obs}}-\nu_{\text{calc}}^*$ cm^{-1} | $\nu_{\text{obs}}-\nu_{\text{calc}}^{**}$ cm^{-1} |
|-----|---|------------------------------------|--------------------------------------|--|---|
| 12 | 3085.62 | | | 3.52 | + 0.31 |
| | | 12.86 | | | |
| 11 | 3072.76 | | 0.83 | 2.78 | + 0.17 |
| | | 13.69 | | | |
| 10 | 3059.07 | | 0.50 | 2.26 | - 0.04 |
| | | 14.19 | | | |
| 9 | 3044.88 | | 0.73 | 1.64 | - 0.02 |
| | | 14.92 | | | |
| 8 | 3029.96 | | 0.75 | 1.14 | 0 |
| | | 15.67 | | | |
| 7 | 3014.29 | | 0.84 | 0.78 | - 0.02 |
| | | 16.51 | | | |
| 6 | 2997.78 | | 0.37 | 0.66 | - 0.18 |
| | | 16.88 | | | |
| 5 | 2980.00 | | 0.78 | 0.36 | - 0.08 |
| | | 17.66 | | | |
| 4 | 2963.24 | | 0.77 | 0.11 | - 0.03 |
| | | 18.43 | | | |
| 3 | 2944.89 | | 0.50 | 0.00 | 0.01 |
| | | 19.03 | | | |
| 2 | 2925.78 | | 0.60 | 0.06 | + 0.04 |
| | | 19.35 | | | |
| 1 | 2906.25 | | 0.50 | + 0.08 | + 0.08 |
| 0 | | | | | |
| -1 | 2865.09 | | | + 0.07 | + 0.07 |
| | | 21.53 | | | |
| -2 | 2843.56 | | - 0.54 | + 0.03 | + 0.01 |
| | | 22.07 | | | |
| -3 | 2821.49 | | - 0.61 | + 0.05 | - 0.01 |
| | | 22.71 | | | |
| -4 | 2798.78 | | - 0.28 | + 0.04 | - 0.10 |
| | | 22.99 | | | |
| -5 | 2775.70 | | - 0.77 | + 0.36 | + 0.08 |
| | | 23.76 | | | |
| -6 | 2752.03 | | - 0.52 | + 0.49 | + 0.03 |
| | | 24.28 | | | |
| -7 | 2727.75 | | - 0.41 | + 0.75 | - 0.01 |
| | | 24.69 | | | |
| -8 | 2703.06 | | - 0.64 | + 1.17 | + 0.03 |
| | | 25.33 | | | |
| -9 | 2677.73 | | - 0.43 | + 1.60 | - 0.02 |
| | | 25.76 | | | |
| -10 | 2651.97 | | - 0.47 | + 2.18 | - 0.04 |
| | | 26.23 | | | |
| -11 | 2625.71 | | - 0.51 | + 2.90 | - 0.05 |
| | | 26.71 | | | |
| -12 | 2599.00 | | | + 3.71 | - 1.12 |

* Calculated from $(I-72): \nu = 2885.90 + 20.577 m - 0.3034 m^2$.** Calculated from: $\nu = 2885.90 + 20.577 m - 0.3034 m^2 - 0.00222 m^3$.

the high revolutionary velocity of the electrons compensates for the mass difference. Because of the *angular momentum of the electrons*, the *direction of the total angular momentum* is not at right angles to the internuclear axis (Fig. 1-17). The deviation increases with the *angular momentum of the electrons* Λ , i. e. with the quantum number Λ of the angular momentum of the electrons about the internuclear axis. The *total angular momentum* J coincides with the component N (the angular momentum of the rotation of the nuclei) only when $\Lambda=0$.

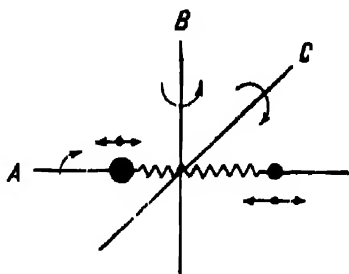


Fig. 1-16 The symmetric top.

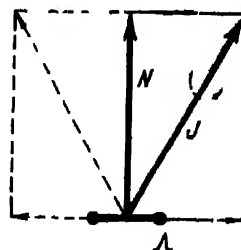


Fig. 1-17 Vector diagram for the symmetric top. The dotted part shows the direction of the vectors when the sense of the angular momentum of the electrons Λ is reversed [1a].

The curved arrow in the figure indicates the sense of rotation of the internuclear axis at a constant angle about the vector J . This motion is called *nutation*. Very often it is mistaken for *precession*, which is the motion of an angular momentum vector under the influence of a force. It is obvious that J is always larger than Λ . The quantum number J can then take the values Λ , $\Lambda+1$, $\Lambda+2$,...

The term of the symmetric top is

$$F(J) = BJ(J+1) + (A-B)\Lambda^2, \quad (1-76)$$

where

$$A = \frac{h^2}{8\pi^2 c I_A} \quad \text{and} \quad B = \frac{h^2}{8\pi^2 c I_B} \quad (1-77)$$

I_A and I_B are moments of inertia about the internuclear axis and about an axis perpendicular to the internuclear axis, respectively. Since I_A is very small, A is much larger than B . The quantum number Λ can take only integral values which are generally small; obviously, for a given electronic state it is constant. Consequently, the energy levels of the symmetric (rigid) top are the same as those of the rigid rotator except that there is a constant shift toward higher values by $(A-B)\Lambda^2$. Levels with J smaller than Λ are absent, since J cannot take these values (Fig. 1-18). Each energy level in

Fig. I-18 actually represents a superimposition of two equal energy states corresponding to the two senses of the angular momentum vector of the electrons in the direction of the internuclear axis. These states, corresponding to the same level, are called *doubly degenerate*.

If we omit the rigidity condition and take into account the simultaneity of rotation and vibration motions, the spectral term for the vibrating symmetric top is

$$F_v(J) = B_v J(J+1) + (A - B_v) \Lambda^2 + D_v J^2(J+1)^2 + \dots \quad (I-78)$$

The selection rules of the symmetric top are given by

$$\Lambda = 0, \Delta J = \pm 1, \quad (I-79)$$

and for

$$\Lambda \neq 0, \Delta J = 0, \pm 1. \quad (I-80)$$

Conditions in (I-79) are the same as for the vibrating rotor. In (I-80), in addition to the *R* and *P* branches due to transitions $\Delta J = \pm 1$ and -1 , respectively, there also appears a third branch, *Q*, due to the now allowed transitions $\Delta J = 0$. The line frequency in the *Q* branch is given by

$$\nu_Q = \nu_0 + F'(J) - F''(J). \quad (I-81)$$

Substitution of (I-76) with B_v and B_0 instead of B gives

$$\nu_Q = \nu_0 + (B_v' - B_v'') \Lambda^2 + (B_v' - B_v'') J + (B_v' - B_v'') J^2. \quad (I-82)$$

Since in the infrared B_v' differs very little from B_v'' , the lines of the *Q* branch give rise to a single stronger absorption around the position ν_0 , which in the case $\Lambda = 0$ does not occur. With the well-known exception of NO, the infrared spectra of all the diatomic molecules studied up to the present time show only *P* and *R* branches, which shows that in these molecules the motions of electrons do not generate an angular momentum about the internuclear axis. Nitrogen oxide is the only heteronuclear diatomic molecule that has an unshared electron in the ground state. This electron gives rise to the angular momentum resulting in the occurrence of the *Q* branch in its infrared spectrum.

1. Intensity distribution in rotation-vibration bands

The factors determining the intensity of an absorption band are the transition probability, the frequency of the absorbed radiation, and the number of molecules in the initial state. Two interesting observations can be made by studying the distribution of line intensities in the rotation-vibration band of the infrared spectrum of hydrogen chloride recorded at different temper-

Fig. I-18
Energy levels
of the symme-
tric top ($\Lambda=2$).
The dotted
lines represent
levels which
do not occur
[1a].

atures (see Fig. I-19). On one hand the band origin ν_0 remains the same and on the other, the shape of the band changes with rising temperature. The intensity of the lines close to the origin decreases, whereas the intensity of the outward lines increases. The result is the flattening and broadening of the band while its initial integrated area remains constant. These observations show that the increase in thermal motion, although fairly large, does not affect the vibrational state; the majority of molecules remain in the fundamental state ($v=0$). However, the thermal energy is large enough to change the rotational state of the molecules, i. e., their distribution in the various rotational levels. With increasing temperature, the higher rotational levels are occupied at the expense of the lower levels. Thus increased intensity of the outward lines is due to the increase in population of the corresponding initial levels, i. e., to a larger number of molecules undergoing the corresponding quantum jump. The intensity (integrated area) of the band remains the same since only the distribution of the molecules in various levels is modified, whereas their total number (i. e. the total number of transitions) remains unchanged.

The number of molecules in a certain vibrational state is given by the classical expression of the Maxwell-Boltzmann rule:

$$dN_E \approx e^{-E/kT} dE,$$

where dN_E is the number of molecules that have an energy between E and dE , k is Boltzmann's constant, and T , the absolute temperature. Using the quantum mechanical expression for the vibration energy, the function $e^{-E/kT}$ becomes $e^{-(v+1/2)hc/\lambda T}$. The exponential decrease of the number of molecules in higher vibrational states ($v \neq 0$) is so fast that under normal conditions one may consider practically all the molecules as being in the fundamental vibrational state ($v=0$).

The number of molecules N_J in a rotational state J corresponding to the initial vibrational state is proportional to $(2J+1)e^{-J(J+1)hc/kT}$. Since the factor $2J+1$ increases linearly with J , the number of molecules in various rotational states does not decrease with increasing rotational quantum number from the very beginning; it first reaches a maximum. The value of J corresponding to this maximum rises with increasing temperature and decreasing rotational constant B . These theoretical observations are in agreement with experimental results. For hydrogen chloride at normal temperature (Figs. I-15 and I-19), the maximum intensity line corresponds to $J \approx 3$. With increasing temperature, the maximum shifts toward positions corresponding to higher J values.

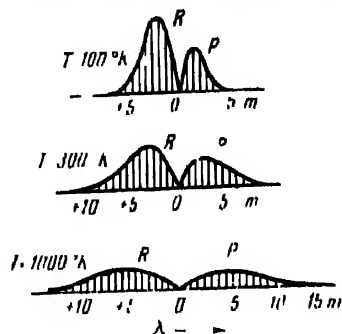


Fig. I-19 Theoretical intensity distribution in the rotation - vibration band of hydrogen chloride [1a].

5. Isotope effect

In infrared spectra of molecules in which one or both atoms are replaced by isotopes, the absorption lines are obviously shifted with respect to the normal positions. These shifts are due exclusively to the *mass effect* (the force constant k determined by electronic motions does not change, since the electronic structure of isotopes is identical). In the following equations, the superscript (i) refers to parameters corresponding to the heavier isotope. The ratio of vibrational frequencies (I-36) is given by

$$\frac{\nu_v^{(i)}}{\nu_v} = \sqrt{\frac{\mu}{\mu^{(i)}}} = \rho. \quad (\text{I-83})$$

Obviously, the "heavier" molecule has the smaller frequency. Equation (I-22) shows that the isotope effect is much stronger when a lighter atom is replaced by its heavier isotope. By substituting (I-83) into (I-44), one finds

$$G = \omega \left(\nu + \frac{1}{2} \right)$$

for the "normal" molecule, and

$$G^{(i)} = \omega^{(i)} \left(\nu + \frac{1}{2} \right) = \rho \omega \left(\nu + \frac{1}{2} \right) \quad (\text{I-84})$$

for the isotopic molecule. Taking into account the anharmonicity of the vibrations, the spectral terms are given by:

$$G(\nu) = \omega_e \left(\nu + \frac{1}{2} \right) - \omega_e x_e \left(\nu + \frac{1}{2} \right)^2 + \omega_e y_e \left(\nu + \frac{1}{2} \right)^3 + \dots, \quad (\text{I-85})$$

$$G^{(i)}(\nu) = \rho \omega_e \left(\nu + \frac{1}{2} \right) - \rho^2 \omega_e x_e \left(\nu + \frac{1}{2} \right)^2 + \rho^3 \omega_e y_e \left(\nu + \frac{1}{2} \right)^3 + \dots$$

Consequently,

$$\omega_e^{(i)} = \rho \omega_e, \quad \omega_e^{(i)} x_e^{(i)} = \rho^2 \omega_e x_e, \quad \omega_e^{(i)} y_e^{(i)} = \rho^3 \omega_e y_e, \dots \quad (\text{I-86})$$

The energy levels of the heavier isotope are lower than in the normal molecule; the difference is more obvious at higher vibrational levels (Fig. I-20).

In rotation the heavier isotope reduces the value of the constant B (ρ is always smaller than unity). The corresponding energy levels are here, too, lower than in the "normal" molecule (Fig. I-21).

$$F = BJ(J+1)$$

$$F^{(i)} = B^{(i)}J(J+1) = \rho^2 BJ(J+1). \quad (\text{I-87})$$

As a first approximation, one can consider that in the rotation-vibration motion the isotope effect is the sum of the rotation and vibration isotope

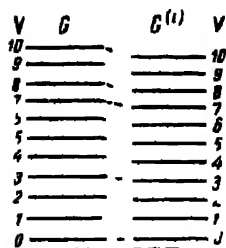


Fig. I-20 Vibrational levels of two isotopic molecules where $\rho = 0.95$ [1a]

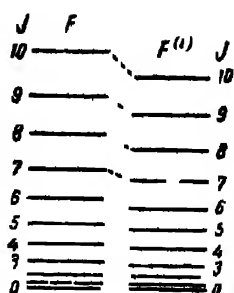


Fig. I-21 Rotational levels of two isotopic molecules where $\rho = 0.95$ [1a].

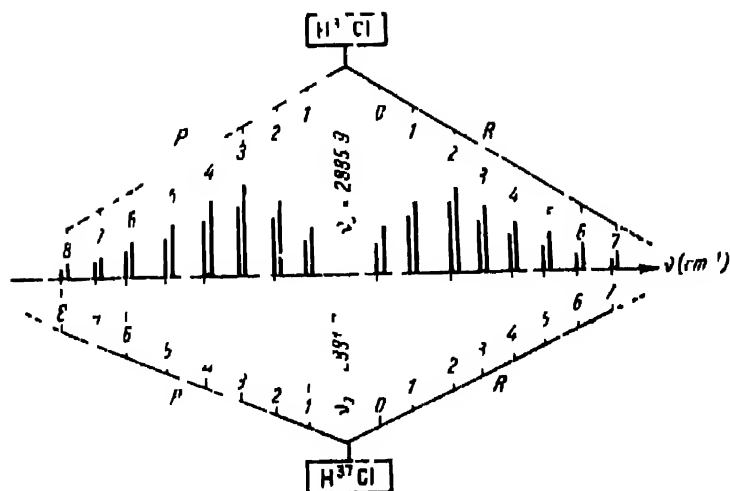


Fig. I-22 Superimposition of rotation-vibration bands in molecules H^{35}Cl and H^{37}Cl

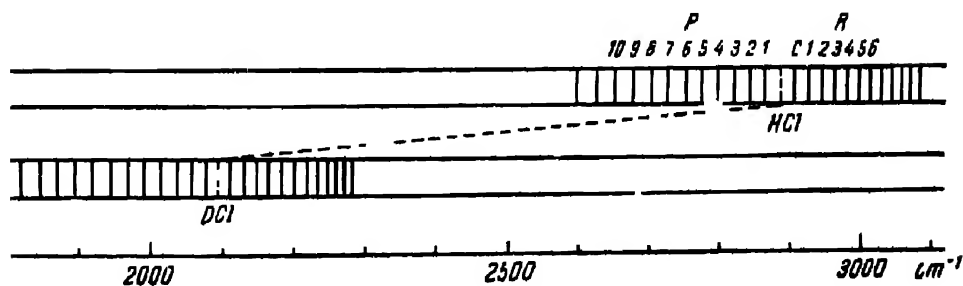
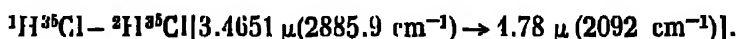


Fig. I-23 Schematic isotopic shifts of rotation-vibration bands H^{35}Cl and H^{37}Cl .

effects described above. In this case not only band frequencies, but also separations of lines are altered. Since rotations and vibrations differ in energy, the isotope vibrational shifts are actually much larger.

The isotope effect was first observed in the hydrogen chloride molecule. The doubling of lines in the infrared spectrum shown in Fig. 1-15 is due to the isotope ^{37}Cl present in the molecule of ordinary hydrogen chloride in a ca. 25% ratio. The lower intensity line in each doublet corresponds to the heavier isotope with a lower vibrational frequency. The pattern of this spectrum results from the superimposition of rotation-vibration spectra of $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$ (Fig. 1-22). Figure 1-23 shows the schematic isotopic shift in the pair



CHAPTER 3

INFRARED SPECTRA OF POLYATOMIC MOLECULES

The mathematical treatment of infrared spectra of polyatomic molecules is much more complicated than that of diatomic molecules since the number of degrees of freedom increases with the number of atoms. A complete analysis of infrared spectra of organic molecules has been performed for only a very small number of simple cases.

Pure rotational spectra of polyatomic molecules practically belong to the microwave region. Current determinations in the infrared deal with vibrational and vibrational-rotational spectra (in cases where the fine structure of bands can be observed). Calculation of vibrational frequency is practically impossible, even for relatively simple molecules. For this reason infrared spectroscopy applied to organic chemistry is for the moment mainly empirical in nature. However, important information can be obtained by correlating theoretical and experimental data, concerning on one hand the close relationship between molecular symmetry and the number of bands active in the infrared and on the other hand, the relationship between the shape of rotation-vibration bands and molecular symmetry.

The activity of rotation and vibration bands in the infrared is determined by the simultaneous change in dipole moment. As a simple we discuss the linear triatomic molecule of carbon dioxide.

Figure 1-24a shows in a conventional way the equilibrium position of each atom. The centers of gravity of the positive and negative charges coincide ($\vec{r}=0$), i.e., the dipole moment ($\vec{M} = -e \cdot \vec{r}$) is zero. Lines *b* and *c* show the extreme positions of the *totally symmetric vibration* ν_1 . In this vibration mode

the centers of gravity of the electric charges coincide at all times and the dipole moment does not change. Consequently, vibration ν_1 is *inactive in the infrared*. It is called the *symmetric stretching* because the vibrations of the oxygen atoms are symmetric with respect to the central carbon atom and move along the lines of the valence bonds. Vibration ν_3 (Fig. 1-24a and e)

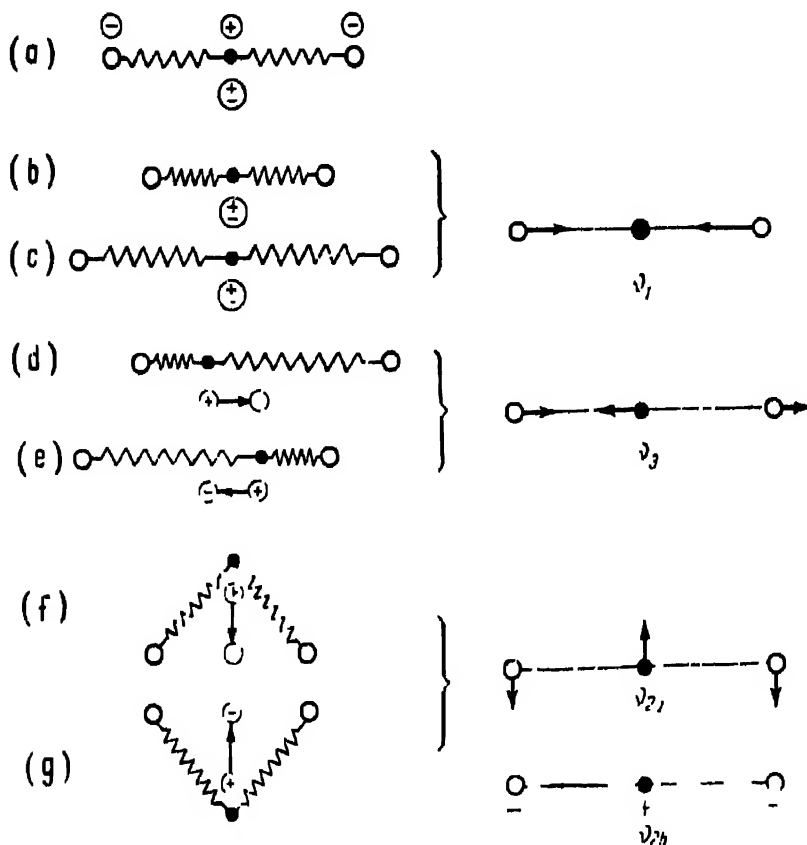


Fig. 1-24 Vibration modes of the carbon dioxide molecule

● carbon atom; ○ oxygen atom; for the ν_{2b} mode the sign + shows the shift of the atom above the plane of the figure and the sign - indicates the shift below this plane

is an *asymmetric stretching vibration*. While one oxygen atom approaches the carbon atom, the other oxygen atom departs. The size and direction of the dipole moment that arises as a result of this motion are given by the extreme positions of the centers of gravity of the electric charges. Thus the asymmetric stretching vibration of the CO_2 molecule is *active in the infrared* because it gives rise to a changing dipole moment. The *deformation vibration* ν_{2a} (in the plane of the paper) involves the alteration of the OCO angle (Fig. 1-24f and g). Giving rise to a changing dipole moment, this vibration mode is also active in the infrared. The molecule can vibrate in the same fash-

ion in a plane perpendicular to the plane of the paper (ν_{2b}). Obviously, the vibration frequency and the change in dipole moment are the same. Consequently, a single band arising from both vibration modes occurs in the infrared. These two vibration modes having the same frequency are called *doubly degenerate*. Thus the carbon dioxide molecule has four possible vibra-

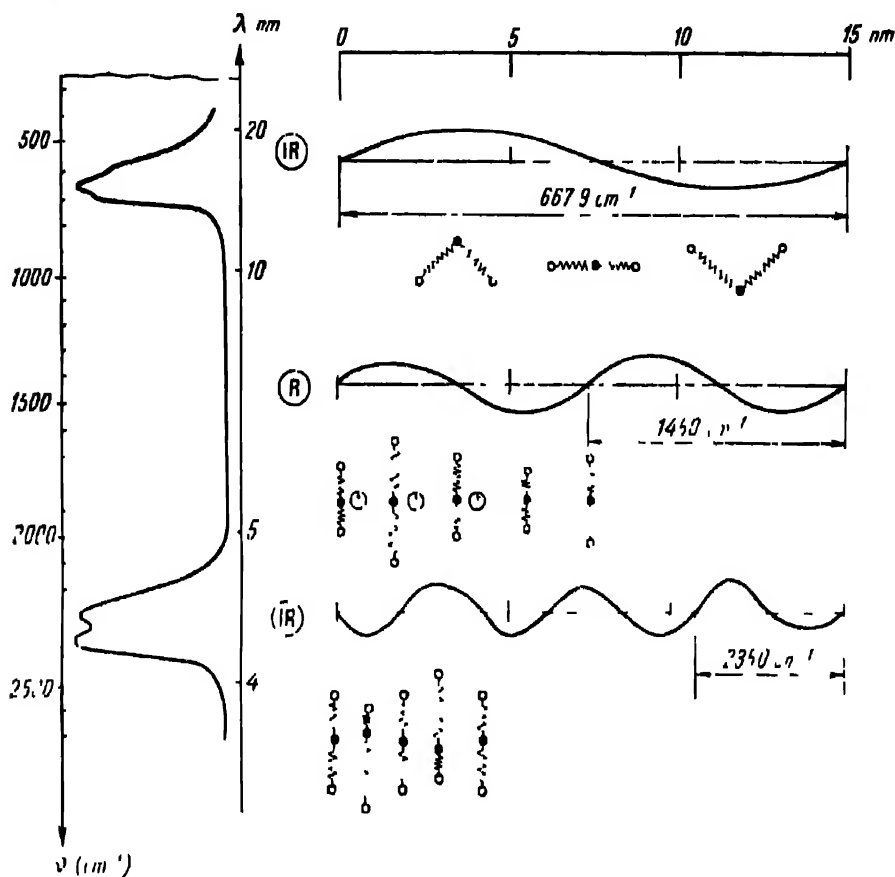


Fig 1-25 Schematic infrared spectrum of carbon dioxide

tional modes, two of which (2_a and 2_b) are *doubly degenerate*. Vibrations ν_2 and ν_3 give rise to a variable dipole moment and are *active in the infrared*. The symmetric stretching is *inactive in the infrared*.

Figure 1-25 shows the schematic infrared spectrum of carbon dioxide and the vibration modes corresponding to the absorption bands and their frequencies.

In the case of totally asymmetric molecules, all the vibration modes are active in the infrared. These molecules do not have degenerate vibration modes. Conversely, polyatomic molecules with high symmetry have more

degenerate vibrational modes and fewer vibrations active in the infrared. In other words, the higher the symmetry of a molecule, the simpler its infrared spectrum. This correlation is of great practical value. The recorded infrared spectrum can give valuable information regarding the structure of the molecule without implying the knowledge of interatomic distances and bond strength or of rotational and vibrational frequencies.

Thus it is very important to find a mathematical correlation between the symmetry of the molecule and the infrared activity of its vibrational modes. There is a simple method which enables one to determine the number of active vibrations and selection rules in the infrared for a molecule of given symmetry. This method does not involve a detailed mathematical treatment (group theory). It is described briefly below, along with the discussion of rotation and vibration spectra of polyatomic molecules.

The first step is to establish the symmetry elements and operations which determine the point group of the actual molecule.

1. Molecular Symmetry

a. **Symmetry elements and symmetry operations.** Nuclei of atoms forming a given molecule may be oriented in space in such a way as to show some common geometric properties with respect to various symmetry elements (axis, plane, etc.) of that molecule. In order to describe these properties we use the examples given in Fig. 1-26.

In Fig. 1-26 *a*, all the atoms in the molecule XY_2 lie in a plane (σ_1). The reflection of the atoms at the plane bisecting the angle YXY -perpendicular to σ_1 does not alter the configuration and the properties of the system. The plane (σ_2) is a *symmetry element* of the molecule XY_2 . It is called a *plane of symmetry*. The reflection of the molecule at the plane of symmetry without change of configuration is called a *symmetry operation*, it is also labeled σ_2 . In the given example, σ_1 is the second plane of symmetry of the molecule.

The molecule XY_2 also has an *axis of symmetry* C_2 situated at the intersection of planes (σ_1) and (σ_2). The symmetry operation corresponding to a symmetry axis C_p is the rotation of the molecule about the axis by an angle $360^\circ/p$ to obtain an identical configuration. The same result is obtained if this operation is carried out two, three, ... n times in succession; in other words, if the molecule rotates about the axis by $360 n/p$ degrees, where $n=1, 2, 3, \dots, p-1$. The corresponding operations are called $C_p, (C_p)^2, (C_p)^3, \dots$. The symbol C suggests the *cyclic* nature of the operation. Of practical value are only cases where $p=2, 3, 4, 5, 6$ and ∞ . The latter is the case of linear molecules (Fig. 1-26 *g, h*) which can rotate about the axis C_∞ by an infinity of angles without altering its configuration. Any axis of symmetry necessarily passes through the center of gravity. If there are several axes of symmetry, they meet in this center. The planes containing the highest-fold axis are called σ_v (vertical). The planes perpendicular to

this axis are called σ_h (horizontal). If the planes or axes of symmetry are defined by the axes of coordinates X , Y , Z they are called σ_{xy} , σ_{xz} , σ_{yz} , C_{yz} , etc. Generally, the highest-fold axis coincides with the z axis of the system.

The molecule Y_2Y_4 (Fig. I-26 b) has three mutually perpendicular symmetry axes C_2 , two planes of symmetry σ_v , and one plane of symmetry σ_h .

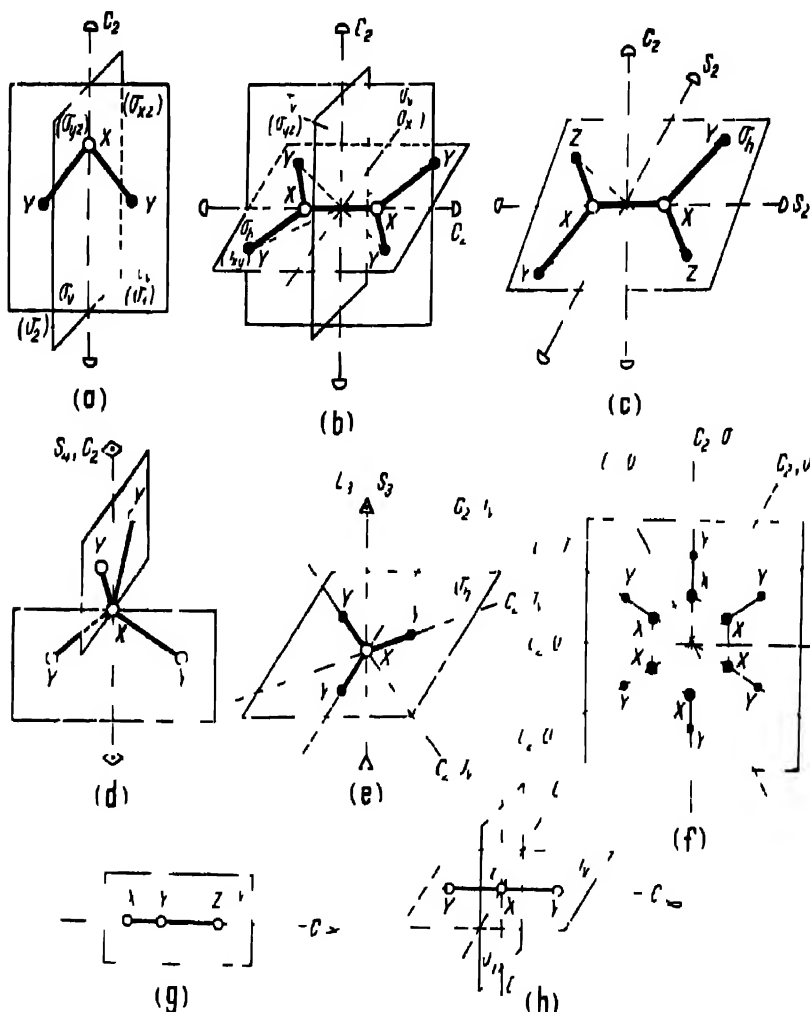


FIG. I-26 Symmetry elements and symmetry operations

If a line is drawn from each atom through the intersection i of the three axes C_2 and continued, it will meet an equal atom at the same distance from the point i but on the opposite side. The point i is called a *center of symmetry*. The corresponding symmetry operation is the reflection of the atoms

at the center of symmetry, called *inversion*. A molecule can have only one center of symmetry. All the atoms of a molecule having a center of symmetry occur in pairs except for the atom situated at the center of symmetry (if the molecule has such an atom).

The molecule $X_2Y_2Z_2$ (Fig. I-26c) has a plane of symmetry σ_h perpendicular to the axis C_2 and a center of symmetry i . If such a molecule would rotate by 180° about one of the S_2 axes, it would not be transformed into itself. For this to occur, rotation has to be followed by reflection at a plane perpendicular to the axis S_2 . It is obvious that the operation S_2 has the same effect as inversion. Any molecule with a C_p axis and a plane σ_h perpendicular to C_p must have an S_p axis. However, the existence of an S_p axis does not necessarily imply the existence of a p -fold axis of symmetry except when p is odd. If p is even, S_p requires the existence of a $p/2$ -fold axis of symmetry; for example, the molecule XY_4 (Fig. I-26d) has an S_4 and a C_2 axis but does not have a C_4 axis. Conversely, the planar molecule XY_3 (Fig. I-26e) has a three-fold rotation-reflection axis and at the same time a C_3 axis and a plane σ_h . If in the molecule represented in Fig. I-26f the atoms Y were alternately above and below the plane formed by the six atoms X , they would have an S_6 axis, but no longer a C_6 axis.

The last symmetry element is the *identity* I . The corresponding operation is to *leave the molecule unchanged*, i.e., to leave unchanged both the configuration and the atomic coordinates. Obviously, the identity is not a true symmetry operation and is applicable to all molecules no matter how unsymmetrical they are. It has been introduced for mathematical reasons.

In general if two symmetry operations are performed in succession, the result is the same as if another possible operation had been performed; for example, in the molecule XY_3 (Fig. I-26e), $(C_3)^3 = I$. If we label the Y atoms by Y_a , Y_b , and Y_c and the planes containing these atoms by σ_a , σ_b , and σ_c (Fig. I-27a) and carry out the operation σ_a twice, the result would be equivalent to the operation I . Thus $(\sigma_a)^2 = I$. In the given example, other equalities are possible as well, for example, $\sigma_b C_3 = \sigma_c$ or $(C_3)^2 = (C_3)^{-1}$. Mathematically, a number of symmetry operations such that the product of any two is again one of them is called a *group*.

There is an almost perfect analogy between products of symmetry operations and algebraic products. The difference is that the order in which symmetry operations are carried out is generally important. Thus if the product $\sigma_b C_3 = \sigma_c$ (see above), then $C_3 \sigma_b = \sigma_a$ (see Fig. I-27).

For any symmetry operation R bringing the molecule from position 1 into position 2, there is a reverse operation R^{-1} bringing the molecule from position 2 back into position 1. In other words, $RR^{-1} = I$. Since $R^{-1}R = I$, $RR^{-1} = R^{-1}R$. The *reverse* of an operation may be the operation itself (e.g., in Fig. I-27a, the reverse of operation σ_b is also σ_b), or it may be another operation (e.g., in the same figure, the *reverse* of operation C_3 is $(C_3)^2$).

All possible symmetry operations in a molecule form a *group of symmetry operations*. They have the following properties:

1. The product of two or several operations is equivalent to one of them.
2. The set always has an identity
3. The product of two or several operations obeys the association rule of multiplication
4. Each symmetry operation within the group has a corresponding reverse operation.

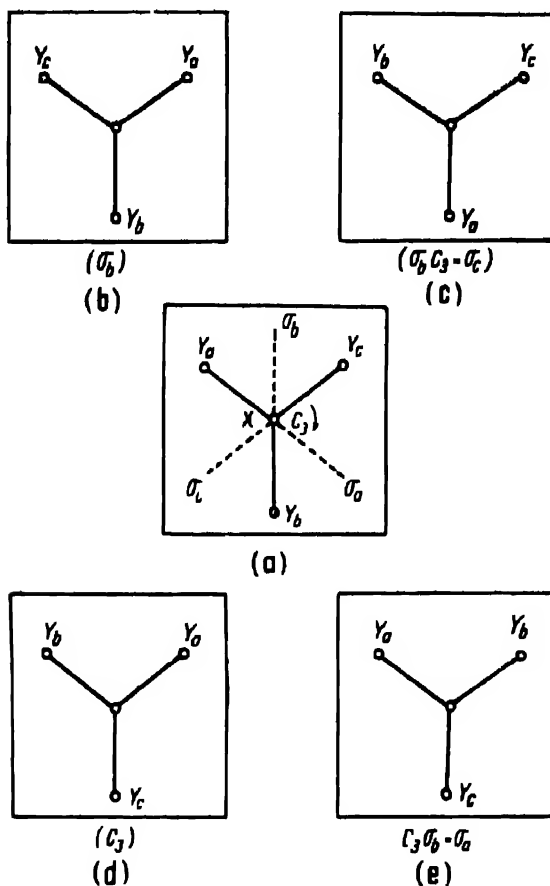


Fig I-27 The molecule X ,
 (a) before carrying out symmetry operations; (b), (c), (d),
 and (e) after carrying out operations σ_b , $\sigma_b C_3$, C_3 , and $C_3 \sigma_b$.

The table shows the group of possible symmetry operations for the molecule represented in Fig. I-26a.

| | 1 | C_3 | σ_1 | σ_2 |
|------------|------------|------------|------------|------------|
| 1 | 1 | C_3 | σ_1 | σ_2 |
| C_3 | C_3 | 1 | σ_2 | σ_1 |
| σ_1 | σ_1 | σ_2 | 1 | C_3 |
| σ_2 | σ_2 | σ_1 | C_3 | 1 |

The group properties can be easily checked

1. $C_2\sigma_1 = \sigma_2$; $C_2I = C_2$, etc.
2. The group has the identity operation I .
3. $C_2(\sigma_1\sigma_2) = (C_2\sigma_1)\sigma_2$.
4. $C_2(C_2)^{-1} = I$.

b. **Point groups.** The number of symmetry operations in a molecule depends on the number and order of the existing symmetry elements. The larger their number, the more symmetric the molecule. As shown above, on one hand, some symmetry elements imply the existence of others and on the other hand, under certain circumstances some elements exclude others. Consequently, only a limited number of combinations of elements or of symmetry operations is possible in a molecule. A combination of possible operations that leaves at least one point of the molecule (the center of gravity) unchanged is called a *point group*. In a *mathematical sense* the point group is a *group*, since it implies symmetry operations which in themselves form a group by respecting the mathematical conditions mentioned above. Group theory shows that there is only a limited number of point groups. This is important since it enables the *classification of millions of organic molecules in a relatively small number of groups depending on the number and nature of their symmetry elements*. The nomenclature used in molecular spectroscopy for point groups is the same as that proposed by A. M. Schönflies in crystallography*. Table I-4 shows the main point groups of organic molecules**.

The simplest group, C_1 , contains totally asymmetric molecules; their only symmetry element is identity.

Molecules having only an axis of symmetry C_p belong to the *cyclic point group* C_p . The corresponding operations are I , (C_p) , $(C_p)^2$, ..., $(C_p)^{p-1}$.

If, in addition, to the main axis of symmetry C_p , the molecule has a number p of C_2 axes perpendicular to the axis C_p , it belongs to the *dihedral point group* D_p . D_2 is generally called V (for the German word Vierergruppe).

If, in addition the molecule has a plane σ_h at right angles to the axis C_p , the corresponding point group is D_{ph} . Obviously, σ_h requires an axis S_p . This group also implies the existence of p axes C_2 . If p is even, a center of symmetry i occurs along with the axis S_p . D_{2h} is often called V_h .

If the molecule has a plane σ_h perpendicular to an axis C_p , and if there is an axis S_p , the molecule belongs to the point group C_{ph} . When $p=1$, the possible operations are I and σ_h . The group C_{1h} is called C_s .

If in addition to the axis C_p the molecule has p vertical planes of symmetry going through C_p , the new group derived from C_p is called C_{pv} . $C_{1v} = C_{1h} = C_s$.

* Unlike molecules, crystals can have only 1, 2, 3, 4 and 6 fold axes (C_5 and C_{∞} are precluded). Consequently in crystallography, there are only 32 point groups corresponding to 32 classes of crystals. Not all crystallographic point groups are encountered in molecular structures, and not all molecular point groups are encountered in crystallography.

** In order to avoid confusion with symmetry elements and operations the symbol of each point group is printed in heavy type.

Table I-4 The most important point groups*

| Point group | Symmetry elements | | | | Examples |
|---------------------|---|--------------------------------|--|-----|---|
| | C_p | S_p | σ | i | |
| C_1 | (C_1) | - | - | - | CHFCIBr, <i>sec.</i> BuOH molecule with asym. C. |
| C_2 | C_{2z} | - | -- | - | H_2O_2 nonplanar (Fig. I-28 a), ClHC=CHCl |
| C_3 | C_{3z} | - | - | -- | $[H_2C-CH_3]$ partially rotated] |
| $D_2 \equiv V$ | $3 C_2 \perp$ | - | - | - | $[H_2C-CH_3]$ nonplanar] |
| D_3 | $3 C_2 \perp C_{3z}$ | - | - | - | $[C_2H_5]$ partially rotated] |
| $S_6 (C_3)$ | - | S_{3z} | - | i | ClBrHC-CHBrCl (<i>anti</i>) (Fig. I-28 b) |
| S_4 | (C_{2z}) | S_{4z} | - | - | - |
| $(C_2) (C_{4h})$ | - | - | σ | - | $H_2C=CHCl$, $C_4H_4Br_4$ (Fig. I-28 g) |
| $(S_4) (C_{4v})$ | - | - | - | - | - |
| C_{2h} | C_{2z} | (S_2) | σ_h | i | <i>trans</i> - ClHC=CHCl (Fig. I-26 c) <i>anti</i> -tricyclooctadiene (C_8H_8) (Fig. I-42) $C_4H_4Br_4$ (Fig. I-28 f) |
| C_{3h} | C_{3z} | (C_3) | σ_h | - | $C^1(NH_2)_3$ (Fig. I-28 c), 1, 3, 5- $C_6H_3(CH_3)_3$ |
| C_{2v} | C_{2z} | - | $2 \sigma_v$ | - | Cl ₂ Cl ₂ <i>syn</i> tricyclooctadiene (C_8H_8) |
| C_{3v} | C_{3z} | - | $3 \sigma_v$ | - | CHCl ₃ , CH ₃ Cl, NH ₃ , $H_2C=CH_2$ |
| C_{4v} | C_{4z} | - | $4 \sigma_v$ | - | $C_4H_4Br_4$ (Fig. I-28 d) |
| C_{6v} | C_{6z} | - | $6 \sigma_v$ | - | $[C_6H_6]$ with C_6 and H_6 in different planes] |
| C_∞ | C_∞ | - | $\infty \sigma_v$ | - | H ₂ CN (Fig. I-26 g), H ₂ C≡CCl, COS |
| $D_{2h} \equiv V_h$ | $3 C_2 \perp$ | - | $3 \sigma_v \perp$ | i | $H_2C=CH_2$ (Fig. I-26 b) |
| D_{3h} | $C_{3z}, 3 C_2 \perp C_{3z}$ | - | $\sigma_h, 3 \sigma_v$ | - | BCl ₃ (Fig. I-26 e); C_2H_6 (eclipsed); 1, 3, 5- $C_6H_3Cl_3$ |
| D_{4h} | $C_{4z}, 4 C_2 \perp C_{4z}$ | (S_8) | $\sigma_h, 4 \sigma_v$ | i | planar cyclobutane, cyclobutadiene |
| D_{5h} | $C_{5z}, 5 C_2 \perp C_{5z}$ | (S_{10}) | $\sigma_h, 5 \sigma_v$ | - | planar sym. cyclopentane |
| D_{6h} | $C_{6z}, 6 C_2 \perp C_{6z}$ | (S_{12}) | $\sigma_h, 6 \sigma_v$ | i | Benzene; C_3Cl_3 |
| $D_{\infty h}$ | $C_\infty, \infty C_2 \perp C_\infty$ | (S_∞) | $\sigma_v, \sigma_h \perp C_\infty$ | i | CO ₂ (Fig. I-26 h); C_2H_2 |
| $D_{2d} \equiv V_d$ | $2 C_2 \perp S_8 (C_{32})$ | S_{12} | $2 \sigma_d$ | - | $C_4H_4Br_4$ (Fig. I-28 e); $H_2C=CH_2$ |
| $D_{3d} (S_{6d})$ | $3 C_2 \perp S_6 (C_{12})$ | S_{12} | $3 \sigma_d$ | i | C_3H_8 staggered; cyclohexane |
| $D_{4d} (S_{8d})$ | $C_4, 4 C_2 \perp C_4 (C_2)$ | $S_8 (C_4)$ | $4 \sigma_d$ | - | S_8 (octagon crown) |
| T | $4 C_3, 3 C_2 \perp$ | - | - | - | $C(CH_3)_4$ asymmetric (Fig. I-29 a) |
| T_d | $4 C_3, 3 C_2 \perp$ | $3 S_4 (C_2)$ | 6σ | - | CH_4 (Fig. I-29 b); CCl_4 ; P_4 ; $C(CH_3)_4$ symmetric |
| O_h | $3 C_4 \perp 4 C_2$ $3 C_2 (C_4), 6 C_2$ | $4 S_6 (C_3)$ $3 S_4 (C_2)$ | $3 \sigma_h \perp C_4$ $6 \sigma_v \perp C_2$ | i | Cubane (Fig. I-29 c); SF_6 $[PtCl_6]^{2-}$ |

* The sign \perp shows that elements of the same kind or different elements are perpendicular ($3 C_2 \perp$) or ($3 C_2 \perp C_{3z}$). Configurations in brackets are improbable.

A molecule that has only an S_p axis, in which p is even, belongs to the point group S_p . The operations associated with this group are I , S_p , $(S_p)^2$, ... $(S_p)^{p-1}$. If p is odd, $S_p = C_{2p}$. If $p = 2$, the point group implies operations I and S_2 . This group is often labeled C_i .

The point group D_{pd} is derived from the group D_p by adding p vertical planes of symmetry bisecting the angles between two successive C_2 axes. The diagonal planes σ_d pass through the axis C_p . When $p = 2$, the group is called V_d .

The point groups mentioned above have a single axis C_p ($p = 1, 2, 3, 4, 5, 6$, or ∞) or different combinations of C_2 axes perpendicular to C_p , as well as planes σ_v , σ_h , or σ_d ; these groups are generally known as *axial point groups*. The majority of molecules (except those with a central atom CH_4 , SiF_4) belong to these groups. Figure 1-28 shows some examples.

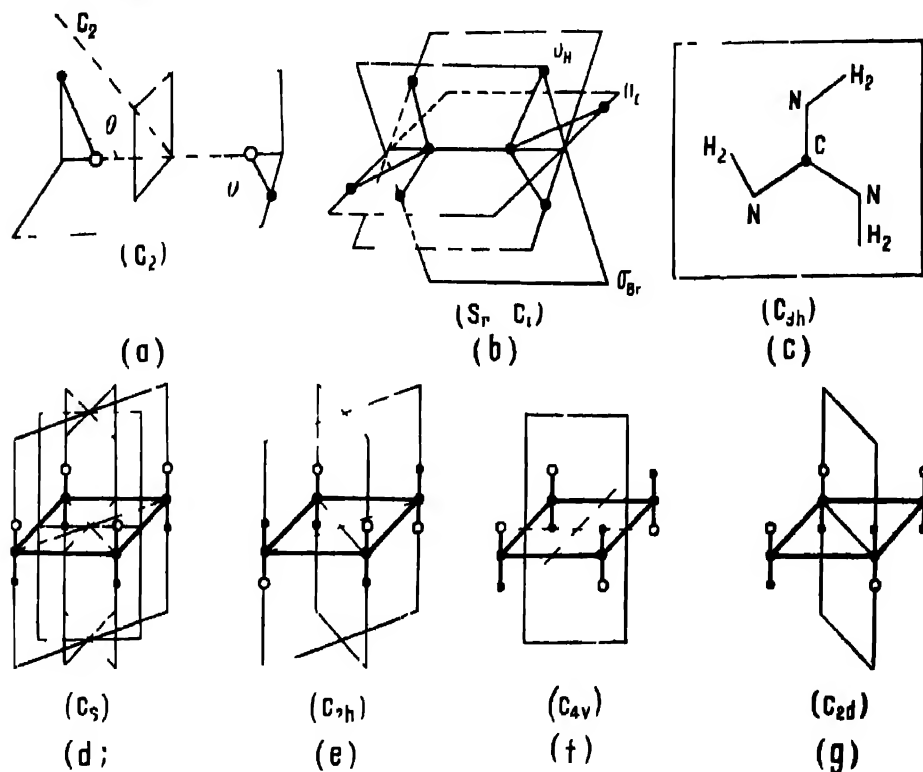


Fig. 1-28 Molecules belonging to axial point groups

Groups with several higher-fold axes of symmetry are called cubic point groups because they form the cubic crystalline systems.

The first cubic group is the tetrahedral point group T , a molecule belonging to this group has four C_3 axes at angles of $109^\circ 28' 16''$ and three mutually perpendicular C_2 axes (see Table 1-4).

The point group T_d also implies a plane of symmetry σ_d going through each pair of C_2 axes (a total of six planes).

The octahedral point group O comprises molecules with three mutually perpendicular axes C_4 and four axes C_3 oriented exactly the same way as the axes C_2 and C_3 in group T . These symmetry elements imply the presence of nine axes C_2 , three of which coincide with the axes C_4 .

A molecule having a center of symmetry in addition to the elements of the group O belongs to the point group O_h . Such a molecule implies, besides the nine C_2 axes, nine planes of symmetry and three axes S_6 coinciding with the axes C_4 .

Figure 1-29 shows schematically three molecules belonging to cubic point groups. Table 1-1 shows the symmetry elements of the most important point groups in studies of molecular structure.

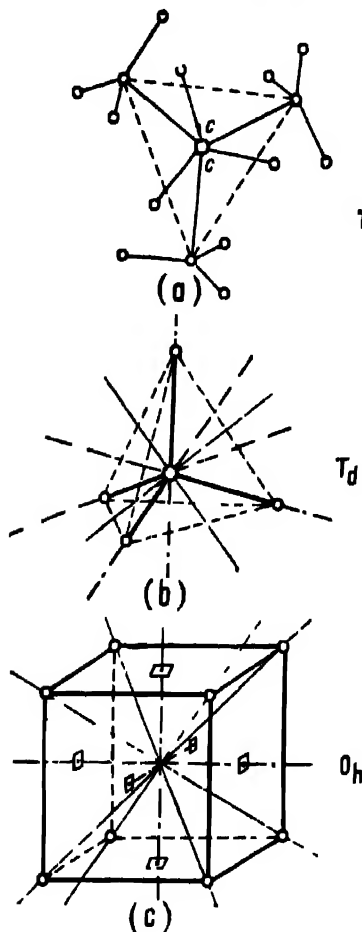


Fig. 1-29 Molecules belonging to cubic point groups:

(a) neopentane, (b) methane, (c) cubane [10]. I_B , I_C is taken into consideration, namely I_B .

2. Rotation of polyatomic molecules. Rotation spectra

As in the case of diatomic molecules, the essential factor determining the rotation spectra of polyatomic molecules is the moment of inertia about the three main axes A , B , C (Fig. 1-16). In symmetric molecules, the axes of symmetry are always the principal axes, and the planes of symmetry are perpendicular to the principal axes.

In the simplest case of linear polyatomic molecules (HCN , C_2H_2 , etc.) only one of the three principal moments of inertia I_A , I_B , I_C is taken into consideration, namely I_B .

The rotational energy of such a system is given by

$$E_{\text{rot}} = \frac{h^2}{8\pi^2 I_B} J(J+1), \quad (\text{I-88})$$

which is similar to (1-24), where $J=0, 1, 2, \dots$ and

$$I_B = \sum_i m_i r_i^2.$$

In this equation, m_i are the atomic masses at a distance r_i from the center of gravity (from the axis of rotation).

The frequency of the rotational transition $J \rightarrow J+1$ is

$$\nu = 1(J+1) - J(J-1) = 2B(J+1). \quad (I-89)$$

The rotational spectrum of linear polyatomic molecules consists of a number of equidistant lines. Their separation (in cm^{-1}) gives the value of B . If one also takes into consideration the centrifugal force, then

$$\nu = 2B(J+1) - 1D_{cf}(J+1)^3, \quad (I-90)$$

where D_{cf} is much smaller than B . Linear polyatomic molecules may belong to the point groups $C_{\infty v}$ and $D_{\infty h}$ (see Fig. I-26 *g* and *h*). Molecules belonging to the group $D_{\infty h}$ with a center of symmetry do not have a rotational spectrum because they do not have a permanent dipole moment.

A molecule in which two out of three principal moments of inertia are equal is a symmetric top. The two equal moments of inertia are called I_B and the third one (about the figure axis) is called I_A . If $I_A < I_B$ the rotator is called *prolate symmetric top*. If $I_A > I_B$ it is called *oblate symmetric top*. The energy levels of the polyatomic symmetric top are given by the same equation as in diatomic molecules in which the quantum number λ is replaced by K . K is the quantum number of the component of the angular momentum about the figure axis

$$I(J, K) = BJ(J+1) - (A-B)K^2 \quad (I-91)$$

A and B are given by (I-77). In the case of polyatomic molecules, A and B are of the same order of magnitude since the moment of inertia I_A results from the rotation of nuclei (not of electrons, see page 51) about the figure axis. As a first approximation, one may consider that there is no electronic angular momentum about this axis. The quantum number K can take values $0, 1, 2, \dots, J$, and is a measure of the rotational velocity of the molecule about the figure axis. The selection rules of the symmetric top with a dipole moment along the figure axis are

$$\Delta J = 1 \text{ and } \Delta K = 0 \quad (I-92)$$

Since K cannot change, the second term in (I-91) vanishes on carrying out the spectral term difference. In this case the frequencies of the symmetric rigid rotator are given by (I-89) and the resulting spectrum consists of a number of equidistant lines as in the case of linear molecules. The rigid rotator is a suitable model for the majority of molecules. If one takes into account the influence of the centrifugal force, the spectral lines are no longer equidistant. Each line with $J > 0$ is split into $J+1$ lines, corresponding to K values. However, the effect is so small that practically it cannot be observed.

As shown above (see Molecular Symmetry, page 59) only molecules with a three- or higher-fold axis can be considered true symmetric tops. C_3 is the only axis of symmetry and the dipole moment must lie in this axis. The molecule CH_3Cl is a typical example of a *prolate symmetric top*. C_6H_6 and BF_3 are examples of *oblate symmetric tops*. Among the few molecules whose far infrared spectra (above $70\ \mu$) have been recorded experimentally, we may quote NH_3 , ND_3 , and PH_3 .

There are also less symmetric or even asymmetric molecules in which two out of three moments of inertia are *accidentally* equal. The spectrum of an *accidental symmetric top* is not as simple as that of a true symmetric top because selection rules are more complicated.

If a molecule has two- or more three-fold or higher-fold axes, it is a spherical top, where $I_A = I_B = I_C$. All molecules with cubic point groups belong to this category (e.g., CH_4 , CCl_4 , etc.). They do not have a permanent dipole moment and consequently do not absorb in the far infrared or microwave region. Only some less symmetric molecules, the so-called *accidental spherical tops*, could have rotational spectra. No such molecules are known at the present time.

It is obvious that most molecules belong to the so-called *asymmetric top* class. These molecules have, at the most, one or several two-fold axes and three different moments of inertia. The theory of rotational energy levels for such molecules involves much more complicated equations.

Again it should be pointed out that the majority of rotation spectra belong to the microwave region.

3. Vibration of polyatomic molecules

a. The mechanical model of the molecule.

In order to describe the vibrational motions of a polyatomic molecule one can use mechanical models consisting of spherical masses proportional to the masses of the atoms involved. These spheres are linked together by simple springs whose lengths and force constants are proportional to the interatomic distances and strengths of the corresponding chemical bonds. The angles in the model are the same as in the actual molecule.

b. Normal vibration modes. Degenerate vibrations. Let us consider first the vibration of a single mass m suspended by a homogeneous elastic bar of rectangular cross section (Fig. 1-30). If the mass is displaced slightly from its equilibrium position in the direction of the axis O_2 and then left to

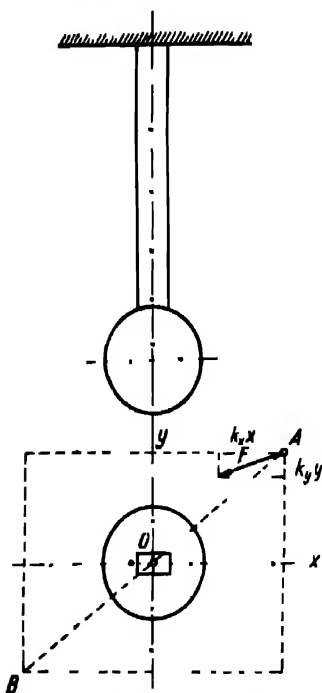


Fig. 1-30 Mass m suspended by an elastic bar [1b].

itself, it will perform a *linear harmonic oscillation* with a frequency of $\nu_x = \frac{1}{2\pi} (k_x/m)^{1/2}$; k_x is the force constant in the O_x direction and $-k_x x$ is the restoring force for the displacement of x . If we repeat the experiment in the O_y direction, the mass will carry out a harmonic oscillation with a frequency $\nu_y = \frac{1}{2\pi} (k_y/m)^{1/2}$. For a rectangular cross section of the bar $\nu_x \neq \nu_y$ ($\nu_y < \nu_x$).

If the mass is displaced in a direction different from x and y , the restoring force F is no longer directed toward O since $k_x \neq k_y$. In this case the mass will carry out a much more complicated motion called the *Lissajous motion*. The components x and y * of this motion are still linear harmonic motions.

$$x = x_0 \cos 2\pi\nu_x' t, \quad y = y_0 \cos 2\pi\nu_y' t, \quad (I-93)$$

where x_0 and y_0 are the coordinates of the initial position A .

The Lissajous motion is the superimposition of two linear harmonic motions of different frequency called *normal vibrations* or *normal modes* of the mass m , x and y are the *normal coordinates*.

The Lissajous motion can be carried out in two ways; if the ratio ν_x'/ν_y' is rational after a certain time, the mass will return to its initial position A and the motion will repeat itself over and over again (Fig. I-31 a); whereas, if the frequency ratio is irrational there is no time after which the motion repeats itself; in the course of time the path of the mass will uniformly cover the whole rectangle whose diagonal is AB (Fig. I-31 b).

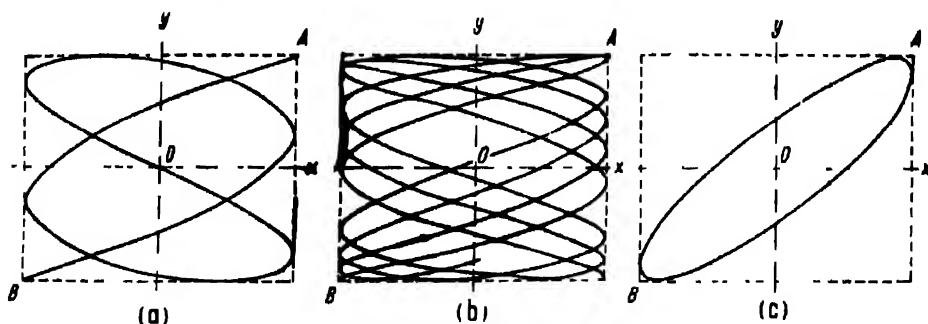


Fig. I-31 Curves representing the Lissajous motion.

If the cross section of the bar is a square or a circle the frequencies of the two components of the motion are equal. Their superimposition results in a linear harmonic motion which under certain circumstances (in-phase

* In theory a component (in the direction of the z axis) may also exist but since ν_z' is much larger than ν_x' and ν_y' , this component is generally not taken into consideration.

vibration of the components) may also be considered as a normal mode and is called *degenerate vibration*.

When there is a phase difference between the two components, the curve is elliptical (Fig. I-31c) or circular (where the amplitudes are equal and the phase difference is 90°). In order to include these modes into the normal vibration, one must give up the condition of phase identity.

Whatever the cross section of the bar, the Lissajous motion is the superimposition of two mutually perpendicular linear harmonic vibrations.

c. **Vibrational coupling. Resonance condition.** If the mass m is excited to forced oscillations by a periodic force of frequency ν_f , the amplitude of the forced oscillation will be the largest when ν_f is equal to ν_x and ν_y . This is the resonance condition (when the vibrational coupling is the largest). When $\nu_f = \nu_x$ the oscillations take place only in the x direction, and when $\nu_f = \nu_y$ they take place only in the y direction, irrespective of the direction of the force (as long as the latter has a non-zero component in the x or y direction).

d. **Vibrations of nuclei in a molecular model.** We now consider the motions of nuclei in the mechanical model of a plane tetrahedral molecule XYZ_2 shown in Fig. I-32. This model shows both the forces of chemical bonds and the weaker field forces (interatomic attraction). If the group YZ_2 is maintained in a rigid position and if X is displaced in a direction other than x , y , or z , a very complicated Lissajous motion will result out of the plane xOy , since the force constant in the z direction is in this case of the same order of magnitude as the other two. Each of the three vibrations forming the Lissajous motion is a linear (normal) harmonic vibration. If we now consider that the YZ_2 group is not rigid, the Lissajous motion of the particle X will show a different figure. Moreover, Y and the two Z particles will be displaced as well. Finally, each of the four particles will have its own Lissajous motion depending on the size and direction of forces that connect it with the other three. There are certain simultaneous displacement modes of the particles resulting in *normal vibrations* as in the case of a single particle. They are characterized by the fact that each particle carries out a simple harmonic motion and that all particles have the same vibrational frequency and move in phase. In other words, each nucleus reaches the respective end point or passes through the equilibrium position at the same time as all the

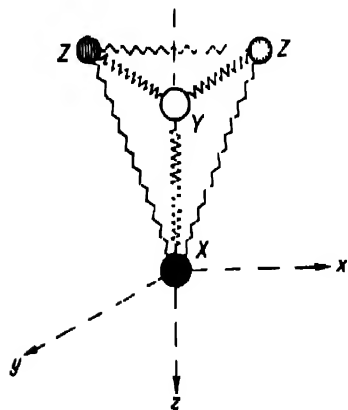


Fig. I-32 The mechanical model of the molecule XYZ_2 [1 b].

others. Amplitudes may be (and generally are) different. Because of Lissajous motions, the vibration of the whole model seems to be fortuitous and random. Actually, it is a superimposition of a certain number of normal vibrations.

Figure I-33 shows schematically the normal vibrational modes of the molecule XYZ_2 . As shown above, if the four nuclei are displaced in the positions indicated by arrows and then released, each one will move back and forth about a certain equilibrium position with the same frequency as the other three in such a way that after each period they will occupy the initial posi-

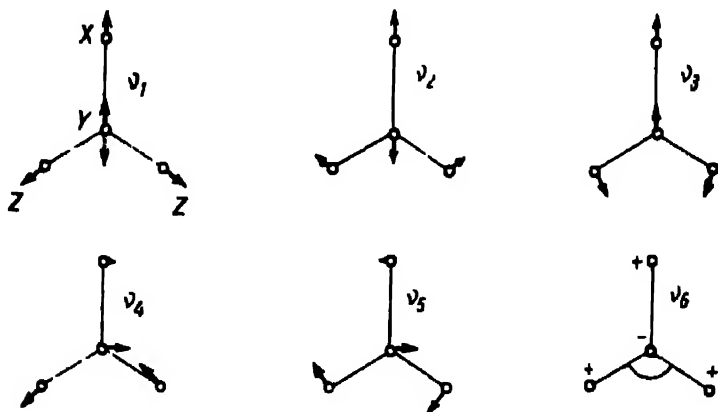


Fig. I-33 Normal vibration modes of the molecule XYZ_2 . The sign shows displacements above the plane of the figure and the - sign, displacements below this plane.

tions. Figure I-33 shows only the arrows representing the initial displacements necessary to perform the normal vibrational modes. The complete oscillation about the equilibrium position is shown only in the case of the central atom in vibration ν_1 by additional dotted arrows. The calculation of these characteristic initial displacements is not shown here. It should be pointed out that the respective arrows are vectors whose relative lengths give the relative velocities and amplitudes of the nuclei. They have to be oriented in such a way that the center of gravity of the molecule does not alter its position. In other words, there is no resultant translation or rotation of the molecule as a whole. Figure I-31 shows normal translation modes T and rotation mode R of the molecule XYZ_2 .

c Degrees of freedom. The number of normal vibrations corresponds to the number of degrees of freedom of the system (molecule). In order to describe the motion of the atoms in a molecule, we may choose, for example, the Cartesian coordinates x_k, y_k, z_k of each nucleus k with respect to a fixed origin. For a molecule with N atoms, we need $3N$ coordinates; consequently, the molecule has $3N$ degrees of freedom. Three are *translational degrees of freedom* and three are *rotational degrees of freedom* (see Fig. I-34).

Therefore, a bent molecule with N atoms can have only $3N - 6$ vibrational degrees of freedom and $3N - 6$ normal vibration modes. Thus the tetra-atomic molecule shown in Fig. I-32 has $3 \times 4 - 6 = 6$ normal vibrational modes shown in Fig. I-33. In linear molecules rotation about the internuclear axis

does not alter any of the coordinates of the atom. Consequently, there are only two rotational degrees of freedom, i.e., linear molecules have $3N - 5$

vibrational degrees of freedom and $3N - 5$ normal vibration modes. The linear triatomic molecule $XY_2(CO_2)$ in Fig. 1-21 has $3 \times 3 - 5 = 4$ normal vibrational modes. Two (ν_{2g} and ν_{2u}) having the same frequency are *doubly degenerate*. Most schematic drawings show only one component of the doubly degenerate vibration.

The above statements can be checked experimentally by means of the stroboscopic effect (examination of the mechanical model in a dark chamber with light which can be turned on and off with variable frequency). In this case, one obtains $3N - 6$ (or $3N - 5$) illumination frequencies when the spherical masses of the model appear motionless to the observer. The phenomenon can be explained in the following way: since the particles move in phase, regardless of their amplitude or direction of motion, they will always be caught together if illuminated with a frequency equal to the corresponding normal vibration mode. If, for symmetry reasons, the model (molecule) had degenerate modes, depending on the degree of degeneracy, we would obtain fewer than $3N - 6$ normal frequencies (e.g., three instead of four in CO_2 , and four instead of nine in CH_4). The mathematical treatment (in classical mechanics) gives the same results.

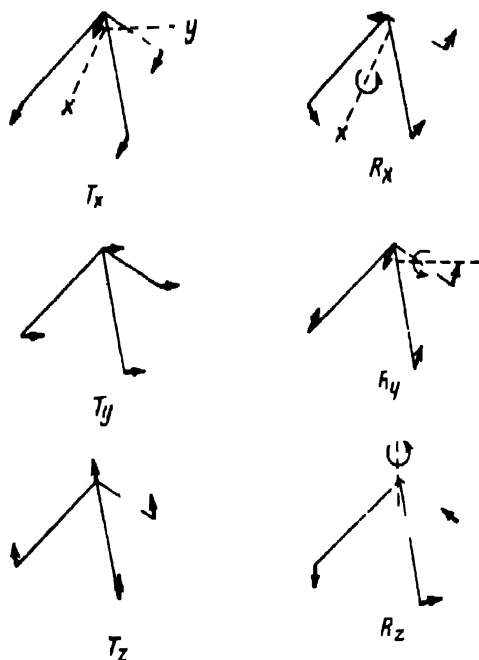


Fig. 1-34 Normal translation and rotation modes of the molecule XY_2 .

1. **Calculation of vibrational frequencies.** In a simple harmonic motion, the displacement s_i of a particle i at time t is given by

$$s_i = s_i^0 \cos(2\pi\nu' t - \varphi) \quad (I-94)$$

where s_i^0 is the amplitude and φ , a phase constant. The acceleration of the particle is

$$a_i = \frac{d^2 s_i}{dt^2} = -1 \pi^2 \nu'^2 s_i^0 \cos(2\pi\nu' t - \varphi) = -1 \pi^2 \nu'^2 s_i \quad (I-95)$$

and the restoring force (mass \times acceleration) is

$$F_i = m_i a_i = -1 \pi^2 \nu'^2 m_i s_i \quad (I-96)$$

This relation holds for the components of the motion in any direction. Thus the restoring force is proportional to $m_i s_i$ at every moment.

If one of the N particles of a system (e. g., particle 1) is displaced from its equilibrium position, it will be returned to this position by a restoring force F^1 proportional to the displacement of the particle; this displacement can be described by means of the three coordinates x_1, y_1, z_1 . If the displacement is sufficiently small (harmonic motion), the three components of the force F^1 are given by

$$\begin{aligned} F_x^1 &= k_{xx}^1 x_1 - k_{xy}^1 y_1 - k_{xz}^1 z_1, \\ F_y^1 &= -k_{yx}^1 x_1 + k_{yy}^1 y_1 - k_{yz}^1 z_1, \\ F_z^1 &= -k_{zx}^1 x_1 - k_{zy}^1 y_1 + k_{zz}^1 z_1, \end{aligned} \quad (1-97)$$

It can happen that two or more solutions are equal to each other. In other words, two or more vibrations can have the same frequency. These vibrations are called *degenerate*. The degree of degeneracy is equal to the number of vibrations with equal frequencies. Practically only second or third degree degeneracies are encountered (*doubly* or *triply degenerate* vibrations). It is obvious that the more symmetric the molecule, the larger the number of degenerate vibrations.

Solving (I-101) for certain values of k_{ij}^I , one obtains the normal frequencies ν' . By substituting the corresponding values of ν' in (I-100) and solving for $x_1, y_1, z_1, x_2, \dots, z_N$, one obtains the form of any one of the normal vibrations.

Since equations (I-100) are homogeneous, one can determine only the ratios of $x_1, y_1, z_1, x_2, \dots, z_N$. Since for a given frequency the ratio $x_1: y_1: z_1: x_2: \dots: z_N$ is independent of time, (I-100) gives the ratio of the components of the amplitudes of the N particles; it also gives the ratio of the velocities at any given moment. The proportionality factors of these ratios expressed in terms of cartesian coordinates are called *normal coordinates*. For the purpose of this book it is not necessary to describe them in detail but only to mention that they are obtained by a reversible linear transformation of the $3N$ cartesian coordinates of the displacement of each particle.

The force constants k_{ij}^I can be determined theoretically only in very few cases (H_2O , H_2 , H_2^+). For other polyatomic molecules, they are obtained by introducing experimental values of the frequencies into the secular equation. Also, there are a number of empirical equations which give satisfactory results.

It is obvious that the solution of the secular equation (I-101) becomes increasingly difficult with the increasing number of atoms in a molecule. Common methods cannot be applied even for $N = 4$ when the secular equation is of the 12th degree. In general, the number of observed frequencies is smaller than the number of force constants. Therefore in order to determine these force constants (and this is one of the main purposes of infrared and Raman spectroscopy), one must find additional equations (like those obtained for the isotope effect) to complete the necessary number of frequencies in the secular equation. The solution of the secular equation is not described here. It can be found in special books mentioned in the references.

The symmetry of the vibrations, associated with the symmetry of the molecules described on page 59 plays an important role in determining the normal vibrational modes. Symmetry properties enable the determination of the number and sometimes even the form of normal vibration modes by a rather simple technique which does not imply the knowledge of the mathematical (group) theory.

The following section describes qualitatively the symmetry of molecular vibrations and the calculation of the number of vibrations active in the infrared based on molecular symmetry.

g. Symmetry of normal vibrations. If a symmetry operation is carried out in a molecule whose nuclei are fixed in an equilibrium position, the

configuration of the molecule does not change. However, if we consider a vibrating molecule, the transformed displacements resulting from the symmetry operation are not necessarily the same as the nontransformed ones.

Normal vibrational modes can show three different behavior patterns with respect to a given symmetry operation: they may remain unchanged; they

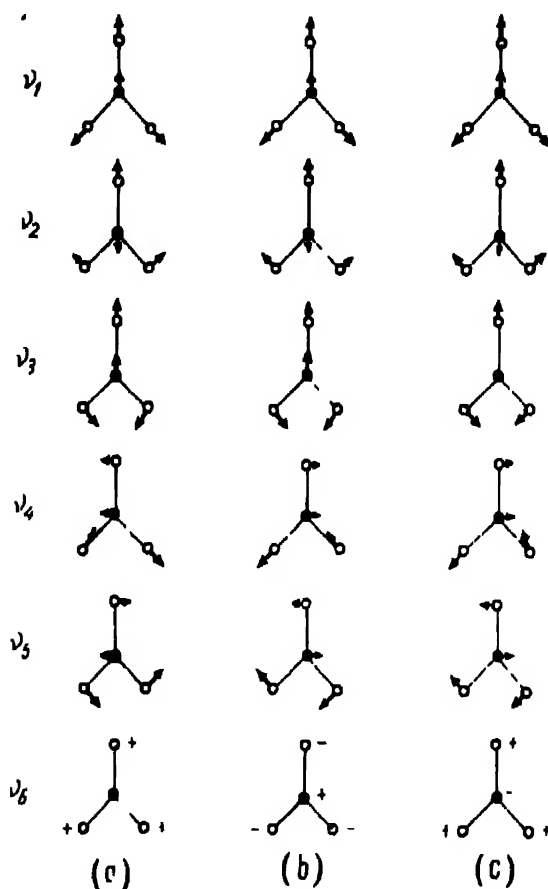


Fig. 1.35 The symmetry of normal vibration modes of the molecule XYZ_3 :

(a) before carrying out the symmetry operation; (b) after the operation C_{2z} ; (c) after the operation σ_{vz} .

may change sign; or they may undergo other changes. Vibrations which do not change their nature as a result of a symmetry operation are called *symmetric* with respect to the given symmetry operation. Vibrations which change sign are called *antisymmetric*. A *nondegenerate* vibration has only these two possibilities since it is characterized by a single ratio for the displacement coordinates of the various atoms. At most the symmetry operation can change

the sign of the respective normal coordinates. Thus, in the molecule XYZ_2 (Fig. 1-35) the modes ν_1 , ν_2 , and ν_3 are symmetric with respect to the operation C_{2z} (rotation of the molecule by 180° about the axis passing through X and Y); whereas ν_4 , ν_5 , and ν_6 are antisymmetric (Fig. 1-35b). ν_1 , ν_2 , ν_3 , and ν_6 are symmetric with respect to σ_{xz} (reflection of the molecule at the plane passing through XY, perpendicular to the plane of the molecule; Fig. 1-35c), whereas in the antisymmetric modes ν_4 and ν_5 , the directions of all displacement vectors are inverted. In other words, the corresponding normal coordinates ξ_4 and ξ_5 change sign (become negative) because of a phase shift of 180° . If one carries out the symmetry operation σ_{yz} (reflection of the molecule at its own plane) (Fig. 1-35a), one can see that the modes ν_1 , ν_2 , ν_3 , ν_4 , ν_5 are symmetric, while ν_6 is antisymmetric with respect to this operation.

It follows that a nucleus that has its equilibrium position in a plane of symmetry can only move *in the plane* if the vibration is symmetric with respect to the plane or *perpendicular* to the plane if the vibration is *antisymmetric*. If the equilibrium position of a nucleus is on an axis of symmetry, the nucleus can move only along this axis if the vibration is symmetric with respect to the axis, or perpendicular to it, if it is antisymmetric. If the molecule has an axis C_p and p is odd, a nondegenerate vibration can only be symmetric since if it were antisymmetric, it would not transform into itself after p rotations by $360/p$ degrees about the axis (i.e. a rotation by 2π). If p is even, the vibration can be symmetric or antisymmetric since it will transform into the original configuration after p rotations by $360/p$ degrees.

The behavior of degenerate vibrations with respect to various symmetry operations is much more complicated. Their description may be found in the treatise mentioned above.

h. Symmetry species of normal vibration modes. Let us consider again the vibrational modes of the molecule XYZ_2 (Fig. 1-35), and let us call $+1$ the symmetric vibrations and -1 the antisymmetric vibrations with respect to a given operation (Table 1-5).

This table is an abstract way of representing the behavior of a vibrating molecule. The set of combinations $+1$ and -1 for each vibrational mode is called an *irreducible representation* since it cannot be reduced to

a simpler form. By combining irreducible representations we can obtain any other *reducible representation*. The results obtained here intuitively can be derived mathematically by means of *group theory* (see references on page 114), where $+1$ and -1 are the *characters* of the matrixes forming the irreducible representation. The matrixes with $+1$ or -1 character are unidimensional.

Table 1-5

| | I | C_{2z} | σ_{xz} | σ_{yz} |
|---------|------|----------|---------------|---------------|
| ν_1 | $+1$ | $+1$ | $+1$ | $+1$ |
| ν_2 | $+1$ | $+1$ | $+1$ | $+1$ |
| ν_3 | $+1$ | $+1$ | $+1$ | $+1$ |
| ν_4 | $+1$ | -1 | -1 | $+1$ |
| ν_5 | $+1$ | -1 | -1 | $+1$ |
| ν_6 | $+1$ | -1 | $+1$ | -1 |

In point groups with a higher-fold axis $C_p (p > 2)$ or with more than one C_p axis ($p \geq 3$), one or several representations may be formed from matrixes with two or three characters, respectively. Actually, the characters represent the transformations of the normal coordinates of the atoms after carrying out the symmetry operations required by the point group of the molecule. Table 1-5 shows that the first three vibrational modes have the same irreducible representation formed from characters +1, +1, +1, +1. One says that they all are of the same *species*. The species of a vibration is in fact its irreducible representation.

The international notation for different *species* based on the behavior of the vibrations with respect to a given symmetry element (operation) is:

A for normal vibrations symmetric with respect to a C_p axis (generally the highest-fold);

B for antisymmetric vibrations with respect to C_p ;

E for doubly degenerate vibrations;

F for triply degenerate vibrations.

If there are several representations of the same type, they are differentiated by numerical subscripts (e.g., $A_1, A_2, \dots, B_1, B_2, \dots$). Their order depends on the symmetry with respect to other elements. If there is a center of symmetry *i*, the behavior of the symmetric vibration is described by the index *g* (from the German word *gerade*) and that of the antisymmetric vibration by the index *u* (from the German word *ungerade*) (e.g., $A_{1g}, A_{1u}, B_{2g}, B_{2u}$, etc.). Symmetric vibrations with respect to a plane of symmetry are labelled ' and antisymmetric vibrations " (e.g., $A'_1, A'_2, B', B'', E', E''$, etc.).

In the case of linear molecules the symbols are:

Σ for nondegenerate vibrations;

Σ^- for nondegenerate vibrations antisymmetric with respect to a plane of symmetry containing the axis of the molecule;

Σ^+ for nondegenerate vibrations antisymmetric with respect to this plane;

Π for doubly degenerate vibrations;

Δ for triply degenerate vibrations.

The above notations have been used to set up tables containing the species and characters of normal vibration modes possible in each point group; for example, Table 1-6 shows the vibrations of the molecule XYZ_2 (point group C_{2v}).

Table 1-6 Species for the point group C_{2v}

| ν_{2v} | <i>I</i> | C_2 | $\sigma_v (xz)$ | $\sigma_v (yz)$ | |
|------------|----------|-------|-----------------|-----------------|------------|
| A_1 | +1 | +1 | +1 | +1 | T_z |
| A_2 | +1 | +1 | -1 | -1 | R_z |
| B_1 | +1 | -1 | +1 | -1 | T_x, R_y |
| B_2 | +1 | -1 | -1 | +1 | T_y, R_x |

In the last column of Table 1-6 are given the translational motions *T* and the rotational motions *R*. Subscripts *x*, *y*, and *z* show that the motion takes

place along or about the corresponding axis. Let us consider as an example the molecule XY_3 (H_2O) (Fig. I-26a) whose vibrational modes are shown in Fig. I-36. One can check the above statements following the effect of the four symmetry operations on all the possible motions. Obviously, all the

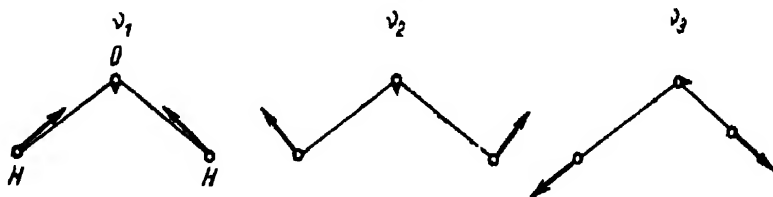


Fig. I-36 Vibration modes of the molecule XY_3 (H_2O)

modes are symmetric with respect to the identity operation. The $|1$ character shows this behavior in all four species given in Column I. Let us consider now the translation T_z of the molecules in the direction of the z axis. This motion is represented by a vector pointing in this direction and having its origin in the center of gravity of the molecule. If one carries out any of the symmetry operations (I , C_{2z} , σ_{xz} , σ_{yz}), this vector does not change. The motion T_z is symmetric with respect to all symmetry operations. Each species must have a $+1$ character. The only species with all characters equal to $+1$ is A_1 . Therefore, the motion T_z must be placed in the first line. Carrying out symmetry operations for T_y , one sees that this motion is symmetric with respect to σ_{yz} and antisymmetric with respect to C_{2z} and σ_{xz} . Consequently, T_y must be placed in the last line containing species B_2 with characters equal to $+1$, -1 , -1 , $+1$. All the other translational and rotational motions of the water molecule can be assigned to the various species of the point group C_{2v} in exactly the same way.

Considering now the normal vibrational modes, one can make similar assignments. Modes ν_1 and ν_2 remain unchanged after carrying out any of the four symmetry operations; in other words, they are symmetric (character $+1$) with respect to these operations. The irreducible representation is the same as for T_z , namely 1 , $+1$, $+1$, $+1$. Therefore the species of the ν_1 and ν_2 modes is A_1 ; they are called A_1 . The vibration ν_3 is symmetric with respect to σ_x (since all the vectors are in the plane σ_x ; see rule on page 77) and antisymmetric with respect to C_{2z} and σ_{yz} . The corresponding characters are -1 , -1 , $+1$, -1 ; consequently, vibration ν_3 belongs to the species B_1 .

Analogously one can find the species of the nondegenerate vibrations in the molecules XY_3 (NI_3) belonging to the point group C_{3v} (Fig. I-37 and Table I-7). Obviously, modes ν_1 and ν_2 are totally symmetric (symmetric with respect to all possible operations within the group) and belong to the species A_1 . The other modes are doubly degenerate. The behavior of degenerate vibrations described by the characters of the corresponding bi- and tridimensional matrixes is complicated and cannot be described here (see references on page 114). We only point out that in various tables the char-

acters in Column I show directly both the degree of degeneracy of vibrations belonging to the respective species and the dimensions of the corresponding matrixes. Also, in each irreducible representation, operations σ_v , σ'_v , σ''_v have the same characters. Such operations form a class of symmetry

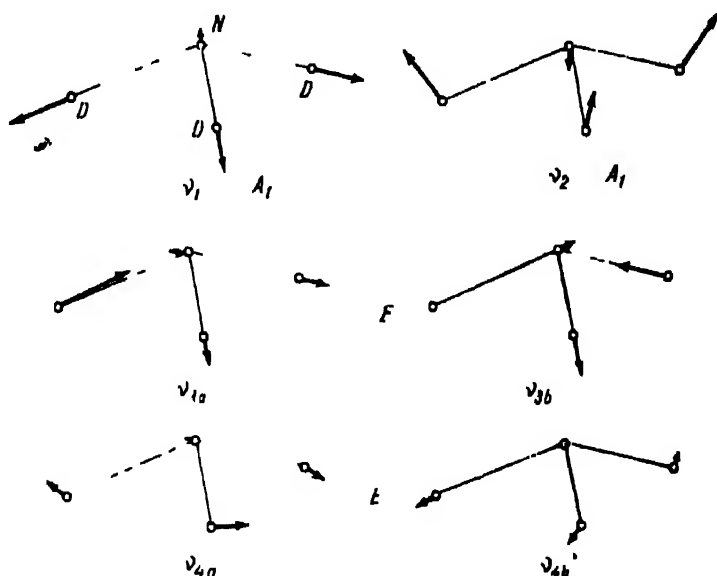


Fig. 1-37 Normal vibration modes of the molecule $XY_3(ND_3)$ [1b]

operations. It suffices to introduce in the tables only the classes of operations. Thus Table I-7 can be rewritten in a simplified form shown in Table I-8. The left upper corner shows the symbol of the point group. It can be seen

Table I-7

| χ_{3v} | I | C_3 | $(C_3)^2$ | σ_v | σ'_v | σ''_v |
|-------------|-----|-------|-----------|------------|-------------|--------------|
| A_1 | +1 | +1 | +1 | +1 | +1 | +1 |
| A_2 | +1 | +1 | +1 | -1 | -1 | -1 |
| E | +2 | -1 | -1 | 0 | 0 | 0 |

that the number of irreducible representations is equal to the number of classes of symmetry operations. The number of symmetry operations (elements) is

obtained by summing the squared characters of the irreducible representations; for example, in Table I-8, the character of A_1 and A_2 is 1, and the character of E is 2. The number of symmetry operations in point group C_{3v} is $1^2 + 1^2 + 2^2 = 6$ (cf. Table I-7).

Table I-8

| χ_{3v} | I | C_3 | σ_v |
|-------------|-----|-------|------------|
| A_1 | +1 | 1 | +1 |
| A_2 | 1 | 1 | 1 |
| E | +2 | -1 | 0 |

1. **Determination of the number of normal vibration modes of a given species.** As shown in the preceding section, if one knows the symmetry of a molecule, one can assign it to a certain point group and thus determine the character (species) of its vibration modes.

If a molecule has a single vibration of a given species, its form can be determined without solving the secular equation (see pag 74).

Even if there are two vibrations of the same species, it is easy to obtain an idea of what these vibrations will be like. Moreover, we can calculate the number of normal vibrations of a given species by applying the rule which limits the number of degrees of freedom of a nucleus placed on one or several symmetry elements (see page 76).

In this respect, the nuclei of a molecule may be divided into certain *sets* according to the following rule: all members of a set are identical and can be transformed into one another by the symmetry operations permitted by the molecule. The members of a set are called *equivalent nuclei*; for example, in the molecule $\text{H}_3\text{C}-\text{CCl}_3$, the nuclei of the three chlorine atoms form a set since they can be transformed into each other by means of the symmetry operation C_3 . The three hydrogen atoms also form a set. The nuclei of the two carbon atoms do not form a set since there is no symmetry operation which would transform them into one another. Each of them may be considered as a monoatomic set. On the other hand, in the ethane molecule the two carbon atoms belong to one set and the six hydrogen atoms to another. Thus we can determine the position (and number) of all nuclei belonging to one set if one knows the position of one nucleus in the set. This nucleus is called the *representative member of the set*. In the examples mentioned above one can observe that the number of members in a set is the largest when the representative nucleus does not lie on a symmetry element (six in the set of the hydrogen nuclei in ethane; three in the sets of hydrogen and chlorine nuclei in 1, 1, 1-trichloroethane). The number of members is smallest when the representative nucleus lies on all symmetry elements (one in the set of carbon nuclei in 1, 1, 1-trichloroethane).

It is also possible to know the displacements of all nuclei in a normal vibrational mode of a given species if we know the displacement of the representative nucleus. In a nondegenerate mode the nucleus of a set can at most contribute three degrees of freedom to each species. This contribution is possible only if the representative nucleus does not lie on any symmetry element. If the representative nucleus lies on a symmetry element, the corresponding set can contribute 2, 1, or 0 degrees of freedom, depending on the symmetry elements and the vibrational species.

These simple rules enable the calculation of the number of degrees of freedom (i.e., the number of normal vibration modes) in a molecule. If one subtracts the number of the corresponding rotational and translational degrees of freedom, one obtains the number of normal vibration modes for a given species. As an illustration, consider a molecule of point group C_{2v} . Table I-6 shows that its $3N-6$ normal vibration modes belong to the species A_1 , A_2 , B_1 , and B_2 (see Table I-9). If the molecule has a representative nucleus

Table I-10 Determination of the number of normal vibrations of each species for the point group C_{2v}

| Species | Degrees of freedom contributed by sets of nuclei | | | Number of normal vibrations | | Vibrations |
|---------|--|---------------|--------------------|-----------------------------|---|-----------------|
| | On no symmetry element | on σ_v | on C_2, σ_v | T | R | |
| A_1 | $3m$ | $2m_v$ | $1 m_0$ | 1 | | $3m+2m_v+m_0-1$ |
| A_2 | $3m$ | $1m_v$ | 0 | | 1 | $3m+m_v-1$ |
| E | $6m$ | $3m_v$ | $1 m_0$ | 1 | 1 | $6m+3m_v+m-2$ |

symmetry. This point group can have three irreducible representations: A_1 , A_2 , E (see Table I-10). If the molecule has a representative nucleus in a σ_v plane, the set contributes six degrees of freedom to species E , i.e., three doubly degenerate modes; m_v such sets contribute $3m_v$ vibrations of the species E (see Table I-10 Column 3.)

If the nucleus lies on no symmetry element, the sets contribute 12 degrees of freedom since the symmetry operation C_2 yields three nuclei with two degrees of freedom each, and each σ_v operation doubles their number. Thus each set in this situation contributes six doubly degenerate modes to species E ; m such sets contribute $6m$ modes (Table I-10, Column 2).

It can be seen from Table I.8 that a nucleus which lies on the C_2 axis can contribute to species E only if its motion is perpendicular (-1) to this axis. In this case it contributes two degrees of freedom, which is equivalent to one doubly degenerate mode (Table I-10, Column 4). In the case of NH_3 or ND_3 ($m=0$, $m_v=1$, $m_0=1$), one obtains two modes A_1 and two modes E (see Fig. I-37); $N=6m+3m_v+m_0=0+3+1=4$. In the case of species E , the number of degrees of freedom is obviously equal to twice the number of normal modes.

The equations used for the determination of normal vibration modes of each species for the principal point groups are given in Table I-11. It contains the point group; the equation for the determination of the total number N of nuclei in the molecule (useful for checking the correct choice of representative nuclei); the species of each group; the activity in the infrared (IR) and Raman (R) (see Appendix III); and equations which sum up the normal vibrations in each species. The following notations have been used: m = number of representative nuclei (sets) which lie on no symmetry element; m_0 = number of representative nuclei which lie on all symmetry elements; m_p = number of representative nuclei which lie on the C_p axis (an additional superscript refers to the orientation of the axis); m'_2 = number of representative nuclei which lie on a C'_2 axis, diagonal with respect to an axis C_2 , perpendicular to C_4 , C_6 , ..., m_v , m_d , m_h = number of representative nuclei which lie on planes of symmetry σ_v , σ_d , σ_h only. If the corresponding plane is determined by the axes of coordinates, the subscripts, v , d , and h are replaced by, xy , xz , yz , respectively. In the case of translational modes (T) and rotational modes (R), the subscripts show the axis involved in these motions.

Table I-11 Number and activity of normal vibration modes

| Point group | Total number of atoms | Species | Activity | | Number of normal vibrations |
|----------------|--|--------------------------|----------|----|---|
| | | | IR | R | |
| C_1 | $N = m$ | A | a | p* | $3m - 6(T_{x,y,z}; R_{x,y,z})$ |
| $C_s (C_{1v})$ | $N = 2m + m_0$ | $A'(\gamma, \delta)$ | a | p* | $3m + 2m_0 - 3(T_{x,y}R_z)$ |
| | | $A''(\gamma)$ | a | dp | $3m + m_0 - 3(T_z, R_{x,y})$ |
| C_2 | $N = 2m + m_0$ | $A(g)$ | a | p* | $3m + m_0 - 2(T_x, R_z)$ |
| | | $B(as)$ | a | dp | $3m + 2m_0 - 4(T_{x,y}, R_{x,y})$ |
| C_{2v} | $N = 4m + 2m_{xz} + 2m_{yz} + m_0$ | $A_1(\pi)$ | a | p | $3m + 2m_{xz} + 2m_{yz} + m_0 - 1(T_z)$ |
| | | $A_2(\gamma, \delta)$ | ia | dp | $3m + m_{xz} + m_{yz} - 1(R_z)$ |
| | | $B_1(\sigma)$ | a | dp | $3m + 2m_{xz} + m_{yz} + m_0 - 2(T_x, R_y)$ |
| | | $B_2(\gamma, as)$ | a | dp | $3m + m_{xz} + 2m_{yz} + m_0 - 2(T_y, R_x)$ |
| C_{2h} | $N = 4m + 2m_h + 2m_g + m_0$ | $A_g(\gamma)$ | ia | p* | $3m + 2m_h + m_g - 1(R_z)$ |
| | | $A_u(\gamma, as)$ | a | i | $3m + m_h + m_g + m_0 - 1(T_z)$ |
| | | $B_g(\gamma, \gamma)$ | ia | dp | $3m + m_h + 2m_g - 2(R_{x,y})$ |
| | | $B_u(as)$ | a | i | $3m + 2m_h + 2m_g + 2m_0 - 2(T_{x,y})$ |
| $D_2 (V)$ | $N = 4m + 2m_{xz} + 2m_{yz} + 2m_{zs} + m_0$ | $A(g)$ | ia | p | $3m + m_{xz} + m_{yz} + m_{zs}$ |
| | | $B_1(as)$ | a | dp | $3m + 2m_{xz} + 2m_{yz} + m_{zs} + m_0 - 2(T_z, R_z)$ |
| | | $B_2(as)$ | a | dp | $3m + 2m_{xz} + m_{yz} + 2m_{zs} + m_0 - 2(T_y, R_y)$ |
| | | $B_3(as)$ | a | dp | $3m + m_{xz} + 2m_{yz} + 2m_{zs} + m_0 - 2(T_x, R_x)$ |
| $D_{2h} (V_h)$ | $N = 8m + 4m_{xy} + 4m_{xz} + 4m_{yz} + 2m_{xz} + 2m_{yz} + 2m_{zs} + m_0$ | $A_g(\pi, \gamma)$ | ia | p | $3m + 2m_{xy} + 2m_{xz} + 2m_{yz} + m_{xz} + m_{yz} + m_{zs} + m_z$ |
| | | $A_u(\gamma, \delta)$ | ia | i | $3m + m_{xy} + m_{xz} + m_{yz}$ |
| | | $B_{1g}(\sigma, s)$ | ia | dp | $3m + 2m_{xy} + m_{xz} + m_{yz} + m_{xz} + m_{yz} - 1(R_z)$ |
| | | $B_{1u}(\gamma, as)$ | a | i | $3m + m_{xy} + 2m_{xz} + 2m_{yz} + m_{xz} + m_{yz} + m_{zs} + m_z + m_0 - 1(T_z)$ |
| | | $B_{2g}(\gamma, \delta)$ | ia | dp | $3m + m_{xy} + 2m_{xz} + m_{yz} + m_{xz} + m_{yz} - 1(R_y)$ |
| | | $B_{2u}(\sigma, as)$ | a | i | $3m + 2m_{xy} + m_{xz} + 2m_{yz} + m_{xz} + m_{yz} + m_{zs} + m_z + m_0 - 1(T_y)$ |
| | | $B_{3g}(\pi, as)$ | ia | dp | $3m + m_{xy} + m_{xz} + 2m_{yz} + m_{xz} + m_{yz} - 1(R_x)$ |
| | | $B_{3u}(\gamma, as)$ | a | i | $3m + 2m_{xy} + 2m_{xz} + m_{yz} + m_{xz} + m_{yz} + m_{zs} + m_z + m_0 - 1(T_x)$ |
| C_3 | $N = 3m + m_0$ | $A(\pi)$ | a | p | $3m + m_0 - 2(T_z, R_z)$ |
| | | $E(\sigma)$ | a | p* | $3m + m_0 - 2(T_{x,y}, R_{x,y})$ |

Table I-11 (continued)

| Point group | Total number of atoms | Species | Activity | | Number of normal vibrations |
|---------------|--------------------------------------|--------------------------|----------|----|---|
| | | | IR | R | |
| C_4 | $N = 4m + m_0$ | A | a | p | $3m + m_0 - 2(T_z, R_z)$ |
| | | B | ia | p* | $3m$ |
| | | E | a | dp | $3m + m_0 - 2(T_{x,y}, R_{x,y})$ |
| | | | | | |
| C_3 | $N = 6m + m_0$ | A | a | p | $3m + m_0 - 2(T_z, R_z)$ |
| | | B | ia | i | $3m$ |
| | | E_1 | a | dp | $3m + m_0 - 2(T_{x,y}, R_{x,y})$ |
| | | E_2 | ia | p | $3m$ |
| | | | | | |
| S_4 | $N = 4m + 2m_2 + m_0$ | A | a | p | $3m + m_2 - 1(R_z)$ |
| | | B | ia | p* | $3m + m_2 + m_0 - 1(T_z)$ |
| | | E | a | dp | $3m + 2m_2 + m_0 - 2(T_{x,y}, R_{x,y})$ |
| | | | | | |
| $C_{3i}(S_6)$ | $N = 6m + 2m_2 + m_0$ | $A_g(\pi, \sigma)$ | ia | p | $3m + m_2 - 1(R_z)$ |
| | | $B_u(\pi, \sigma)$ | a | i | $3m + m_2 + m_0 - 1(T_z)$ |
| | | $E_{1u}(\sigma, \sigma)$ | a | i | $3m + m_2 + m_0 - 1(T_{x,y})$ |
| | | $E_{2g}(\sigma, \sigma)$ | ia | p* | $3m + m_2 - 1(R_{x,y})$ |
| | | | | | |
| D_3 | $N = 6m + 3m_2 + 2m_3 + m_0$ | $A_1(\pi)$ | ia | p | $3m + m_2 + m_3$ |
| | | $A_2(\pi)$ | a | i | $3m + 2m_2 + m_2 + m_0 - 2(T_z, R_z)$ |
| | | $E(\sigma)$ | a | p* | $6m + 3m_2 + 2m_3 + m_0 - 2(T_{x,y}, R_{x,y})$ |
| | | | | | |
| D_4 | $N = 8m + 4m_2 + 4m_3 + 2m_4 + m_0$ | A_1 | ia | p | $3m + m_2 + m_3 + m_4$ |
| | | A_2 | a | i | $3m + 2m_2 + 2m_3 + m_4 + m_0 - 2(T_z, R_z)$ |
| | | B_1 | ia | p* | $3m + m_2 + 2m_3$ |
| | | B_2 | ia | dp | $3m + 2m_2 + m_2$ |
| | | E | a | dp | $6m + 3m_2 + 3m_3 + 2m_4 + m_0 - 2(T_{x,y}, R_{x,y})$ |
| | | | | | |
| D_6 | $N = 12m + 6m_2 + 6m_3 + 2m_4 + m_0$ | A_1 | ia | p | $3m + m_2 + m_3 + m_4$ |
| | | A_2 | a | i | $3m + 2m_2 + 2m_3 + m_4 + m_0 - 2(T_z, R_z)$ |
| | | B_1 | ia | i | $3m + m_2 + 2m_3$ |
| | | B_2 | ia | i | $3m + 2m_2 + m_2$ |
| | | E_1 | a | dp | $6m + 3m_2 + 3m_3 + 2m_4 + m_0 - 2(T_{x,y}, R_{x,y})$ |
| | | E_2 | ia | p* | $6m + 3m_2 + 3m_3$ |
| | | | | | |
| C_{3v} | $N = 6m + 3m_2 + m_0$ | $A_1(\pi)$ | a | p | $3m + 2m_2 + m_0 - 1(T_z)$ |
| | | $A_2(\pi)$ | ia | i | $3m + m_2 - 1(R_z)$ |
| | | $E(\sigma)$ | a | p* | $6m + 3m_2 + m_0 - 2(T_{x,y}, R_{x,y})$ |
| | | | | | |
| C_{4v} | $N = 8m + 4m_2 + 4m_3 + m_0$ | A_1 | a | p | $3m + 2m_2 + 2m_3 + m_0 - 1(T_z)$ |
| | | A_2 | ia | i | $3m + m_2 + m_3 - 1(R_z)$ |
| | | B_1 | ia | p* | $3m + 2m_2 + m_3$ |
| | | B_2 | ia | dp | $3m + m_2 + 2m_3$ |
| | | E | a | dp | $6m + 3m_2 + 3m_3 + m_0 - 2(T_{x,y}, R_{x,y})$ |
| | | | | | |

Table I-11 (continued)

| Point group | Total number of atoms | Species | Activity IR R | Number of normal vibrations |
|-------------------------------|-------------------------------------|------------------|------------------|---|
| C_{3v} | $N = 10m + 5m_i + m_o$ | A_1 | a p | $3m + 4m_i + m_o - 1(T_z)$ |
| | | A_2 | ia i | $3m + m_o - 1(R_z)$ |
| | | E_1 | a dp | $6m + 3m_i + m_o - 2(T_{x,y}, R_{x,y})$ |
| | | E_2 | ia p | $6m + 3m_i$ |
| C_{3v} | $N = 12m + 6m_i + 6m_d + m_o$ | A_1 | a p | $3m + 2m_i + 2m_d + m_o - 1(T_z)$ |
| | | A_2 | ia i | $3m + m_i + m_d - 1(R_z)$ |
| | | E_1 | ia i | $3m + 2m_i + m_d$ |
| | | E_2 | ia i | $3m + m_i + 2m_d$ |
| | | E_1 | a dp | $6m + 3m_i + 3m_d + m_o - 2(T_{x,y}, R_{x,y})$ |
| | | E_2 | ia p | $6m + 3m_i + 3m_d$ |
| $C_{\infty v}$ | $N - m_o$ | $\Sigma^+(v)$ | a p | $m_o - 1(T_z, R_z)$ |
| | | $\Pi(\delta)$ | a dp | $m_o - 2(T_{x,y}, R_{x,y})$ |
| | | $\Delta(\delta)$ | ia p | 0 |
| C_{3h} | $N = 6m + 3m_h + 2m_i + m_o$ | $A'(\pi)$ | ia p | $3m + 2m_h + m_i - 1(R_z)$ |
| | | $A''(\pi)$ | a i | $3m + m_h + m_i + m_o - 1(T_z)$ |
| | | $E'(\sigma)$ | a p* | $3m + 2m_h + m_i + m_o - 1(T_{x,y})$ |
| | | $E''(\sigma)$ | ia dp | $3m + m_h + m_i - 1(R_{x,y})$ |
| C_{4h} | $N = 8m + 4m_h + 2m_d + m_o$ | A_g | ia p | $3m + 2m_h + m_d - 1(R_z)$ |
| | | A_u | a i | $3m + m_h + m_d + m_o - 1(T_z)$ |
| | | B_g | ia p* | $3m + 2m_h$ |
| | | B_u | ia i | $3m + m_h$ |
| | | E_g | ia dp | $3m + m_h + m_d - 1(R_{x,y})$ |
| | | E_u | a i | $3m + 2m_h + m_d + m_o - 1(T_{x,y})$ |
| C_{6h} | $N = 12m + 6m_h + 2m_d + m_o$ | A_g | ia p | $3m + 2m_h + m_d - 1(R_z)$ |
| | | A_u | a i | $3m + m_h + m_d + m_o - 1(T_z)$ |
| | | B_g | ia i | $3m + m_h$ |
| | | B_u | ia i | $3m + 2m_h$ |
| | | E_{1g} | ia dp | $3m + m_h + m_d - 1(R_{x,y})$ |
| | | E_{1u} | a i | $3m + 2m_h + m_d + m_o - 1(T_{x,y})$ |
| | | E_{2g} | ia p* | $3m + 2m_h$ |
| | | E_{2u} | ia i | $3m + m_h$ |
| D_{2d} (V_d, S_{4v}) | $N = 8m + 4m_d + 4m_i + 2m_d + m_o$ | A_1 | ia p | $3m + 2m_d + m_i + m_d$ |
| | | A_2 | ia i | $3m + m_d + 2m_i - 1(R_z)$ |
| | | B_1 | ia p* | $3m + m_d + m_i$ |
| | | B_2 | a dp | $3m + 2m_d + 2m_i + m_d + m_o - 1(T_z)$ |
| | | E | a dp | $6m + 3m_d + 3m_i + 2m_d + m_o - 2(T_{x,y}, R_{x,y})$ |

Table I-11 (continued)

| Point group | Total number of atoms | Species | Activity | | Number of normal vibrations |
|---------------|--|-------------------|----------|----|--|
| | | | IR | R | |
| $D_{3d}(S_6)$ | $N = 12m + 6m_d + 6m_a + 2m_b + m_0$ | $A_{1g}(\pi, s)$ | 1a | p | $3m + 2m_d + m_b + m_0$ |
| | | $A_{1g}(\pi, as)$ | 1a | i | $3m + m_d + m_b$ |
| | | $A_{2g}(\pi, s)$ | 1a | i | $3m + m_d + 2m_b - 1(R_z)$ |
| | | $A_{2g}(\pi, as)$ | a | i | $3m + 2m_d + 2m_b + m_0 + m_0 - 1(T_z)$ |
| | | $E_g(\sigma, s)$ | 1a | p* | $6m + 3m_d + 3m_b + m_0 - 1(R_{x,y})$ |
| | | $E_g(\sigma, as)$ | a | i | $6m + 3m_d + 3m_b + m_0 + m_0 - 1(T_{x,y})$ |
| D_{4d} | $N = 16m + 8m_d + 8m_a + 2m_b + m_0$ | A_1 | 1a | p | $3m + 2m_d + m_b + m_0$ |
| | | A_2 | 1a | i | $3m + m_d + 2m_b - 1(R_z)$ |
| | | B_1 | 1a | i | $3m + m_d + m_b$ |
| | | B_2 | a | i | $3m + 2m_d + 2m_b + m_0 + m_0 - 1(T_z)$ |
| | | E_1 | a | i | $6m + 3m_d + 3m_b + m_0 + m_0 - 1(T_{x,y})$ |
| | | E_2 | 1a | p* | $6m + 3m_d + 3m_b$ |
| | | E_3 | 1a | dp | $6m + 3m_d + 3m_b + m_0 - 1(R_{x,y})$ |
| D_{3h} | $N = 12m + 6m_l + 6m_h + 3m_a + 2m_b + m_0$ | $A'_1(\pi)$ | 1a | p | $3m + 2m_v + 2m_h + m_b + m_0$ |
| | | $A'_2(\pi)$ | 1a | i | $3m + m_v + m_h$ |
| | | $A'_3(\pi)$ | 1a | i | $3m + m_v + 2m_h + m_b - 1(R_z)$ |
| | | $A''_3(\pi)$ | a | i | $3m + 2m_v + m_h + m_b + m_0 + m_0 - 1(T_z)$ |
| | | $E'(\sigma)$ | a | p* | $6m + 3m_v + 4m_h + 2m_b + m_b + m_0 - 1(T_{x,y})$ |
| | | $E''(\sigma)$ | 1a | dp | $6m + 3m_v + 2m_h + m_b + m_b - 1(R_{x,y})$ |
| D_{4h} | $N = 16m + 8m_l + 8m_d + 8m_h + 4m_a + 4m'_2 + 2m_b + m_0$ | A_{1g} | 1a | p | $3m + 2m_v + 2m_d + 2m_h + m_b + m'_2 + m_0$ |
| | | A_{1u} | 1a | i | $3m + m_v + m_d + m_h$ |
| | | A_{2g} | 1a | i | $3m + m_v + m_d + 2m_h + m_b + m_b - 1(R_z)$ |
| | | A_{2u} | a | i | $3m + 2m_v + 2m_d + m_b + m_b + m'_2 + m_0 + m_0 - 1(T_z)$ |
| | | B_{1g} | 1a | p* | $3m + 2m_v + m_d + 2m_h + m_b + m'_2$ |
| | | B_{1u} | 1a | i | $3m + m_v + 2m_d + m_h + m'_2$ |
| | | B_{2g} | 1a | dp | $3m + m_v + 2m_d + 2m_h + m_b + m'_2$ |
| | | B_{2u} | 1a | i | $3m + 2m_v + m_d + m_h + m_b$ |
| | | E_g | 1a | dp | $6m + 3m_v + 3m_d + 2m_h + m_b + m'_2 + m_0 - 1(R_{x,y})$ |
| | | E_u | a | i | $6m + 3m_v + 3m_d + 4m_h + 2m_b + 2m_b + m_b + m_0 - 1(T_{x,y})$ |

Table L-11 (continued)

| Point group | Total number of atoms | Species | Activity | | Number of normal vibrations |
|----------------|--|-------------------------------|----------|----|--|
| | | | IR | R | |
| D_{3h} | $N = 20m + 10m_i + 10m_h + 5m_s + 2m_o + m_o$ | A'_1 | 1a | p | $3m + 2m_o + 2m_h + m_s + m_i$ |
| | | A'_2 | 1a | i | $3m + m_o + m_h$ |
| | | A'_3 | 1a | i | $3m + m_o + 2m_h + m_s - 1(R_s)$ |
| | | A''_2 | a | i | $3m + 2m_o + m_h + m_s + m_i + m_o - 1(T_{x,y})$ |
| | | E'_1 | a | i | $6m + 3m_o + 4m_h + 2m_s + m_i + m_o - 1(T_z)$ |
| | | E''_1 | 1a | dp | $6m + 3m_o + 2m_h + m_s + m_i - 1(R_{x,y})$ |
| | | E''_2 | 1a | p* | $6m + 3m_o + 4m_h + 2m_s$ |
| D_{3h} | $N = 24m + 12m_i + 12m_h + 12m_s + 6m_o + 6m_o + 2m_o + m_o$ | A_{1g} | 1a | p | $3m + 2m_o + 2m_h + 2m_s + m_i + m_o + m_o$ |
| | | A_{1u} | 1a | i | $3m + m_o + m_h + m_s$ |
| | | A_{2g} | 1a | i | $3m + m_o + m_h + 2m_s + m_i + m_o - 1(R_z)$ |
| | | A_{2u} | a | i | $3m + 2m_o + 2m_h + m_h + m_i + m_o - 1(T_z)$ |
| | | B_{1g} | 1a | i | $3m + m_o + 2m_h + m_s + m_i$ |
| | | B_{1u} | 1a | i | $3m + 2m_o + m_h + 2m_s + m_i + m_o$ |
| | | B_{2g} | 1a | i | $3m + 2m_o + m_h + m_s + m_i$ |
| | | B_{2u} | 1a | i | $3m + m_o + 2m_h + 2m_s + m_i + m_o$ |
| | | L_{1g} | 1a | dp | $6m + 3m_o + 3m_h + 2m_s + m_i + m_o - 1(R_{x,y})$ |
| | | L_{1u} | a | i | $6m + 3m_o + 3m_h + 4m_s + 2m_i + 2m_o + m_o - 1(T_{x,y})$ |
| | | L_{2g} | 1a | p* | $6m + 3m_o + 3m_h + 4m_s + 2m_i + 2m_o$ |
| | | L_{2u} | 1a | i | $6m + 3m_o + 3m_h + 2m_s + m_i + m_o$ |
| $D_{\infty h}$ | $N = 2m_{\infty} + m_o$ | $\Sigma^+ g(\gamma, s)$ | 1a | p | m_{∞} |
| | | $\Sigma^+ u(\nu, \sigma \nu)$ | a | i | $m_{\infty} + m_o - 1(T_z, R_z)$ |
| | | $\Pi g(\delta, s)$ | 1a | dp | $m_{\infty} - 1(R_{x,y})$ |
| | | $\Pi u(\delta, \sigma s)$ | a | i | $m_{\infty} + m_o - 1(T_{x,y})$ |
| | | $\Delta g(\delta, s)$ | 1a | p* | 0 |
| T | $N = 12m + 6m_s + 4m_s + m_o$ | A | 1a | p | $3m + m_s + m_s$ |
| | | E | 1a | dp | $3m + m_s + m_s$ |
| | | F | a | dp | $9m + 5m_s + 3m_s + m_o - 2(T_{x,y}, s, R_{x,y}, s)$ |
| T_d | $N = 24m + 12m_h + 6m_s + 4m_s + m_o$ | A_1 | 1a | p | $3m + 2m_h + m_s + m_s$ |
| | | A_2 | 1a | i | $3m + m_h$ |
| | | E | 1a | dp | $6m + 3m_h + m_s + m_s$ |
| | | F_1 | 1a | i | $9m + 4m_h + 2m_s + m_s - 1(R_{x,y}, s)$ |
| | | F_2 | a | dp | $9m + 5m_h + 3m_s + 2m_s + m_o$ |

Table I-11 (continued)

| Point group | Total number of atoms | Species | Activity | | Number of normal vibrations |
|-------------|---|----------|----------|----|--|
| | | | IR | R | |
| O_h | $N = 48m + 24m_h + 24m_d + 12m_s + 8m_a + 6m_i + m_0$ | A_{1g} | ia | p | $3m + 2m_h + 2m_d + m_s + m_a + m_i$ |
| | | A_{1u} | ia | i | $3m + m_h + m_d$ |
| | | A_{2g} | ia | i | $3m + 2m_h + m_d + m_s + m_a$ |
| | | A_{2u} | ia | i | $3m + m_h + 2m_d + m_s + m_a$ |
| | | E_g | ia | dp | $6m + 4m_h + 3m_d + 2m_s + m_a + m_i$ |
| | | E_u | ia | i | $6m + 2m_h + 3m_d + m_s + m_a$ |
| | | F_{1g} | ia | i | $9m + 4m_h + 4m_d + 2m_s + m_a + m_i - 1(R_{\sigma}, \gamma, z)$ |
| | | F_{1u} | a | i | $9m + 5m_h + 5m_d + 3m_s + 2m_a + 2m_i + m_0 - 1(T_{\sigma}, \gamma, z)$ |
| | | F_{2g} | ia | dp | $9m + 4m_h + 5m_d + 2m_s + 2m_a + m_i$ |
| | | F_{2u} | ia | i | $9m + 5m_h + 4m_d + 2m_s + m_a + m_i$ |

In the column entitled "Activity" IR=infrared, a=active, ia=inactive, R=Raman, p=polarized, p*=partially polarized, dp=depolarized, i=forbidden. The coefficients in Column N show the number of nuclei in the set. Along with the symbols of the species, the following commonly used notations are given: ν for the *stretching vibrations* and δ for *deformation vibrations*. If the molecule has a characteristic plane of symmetry (e.g., the plane of the molecule) the deformation vibrations are called δ when the motion of the dipole moment is parallel to the plane and γ when it is perpendicular to it. If the transition moment is parallel to a special symmetry element (axis or plane) involving several identical valencies, the vibrations are called $\nu\pi$ or $\delta\pi$. If the moment is perpendicular to the symmetry element, the vibrations are called $\nu\sigma$ or $\delta\sigma$; s = symmetric; a = antisymmetric. To illustrate the use of Table I-11, we consider the four isomers of tetrabromocyclobutane schematically shown in Fig. I-39.

One must determine the point groups of the molecules. Considering that the cyclobutane skeleton is planar, the symmetry of these molecules is C_{4v} (I), D_{2d} (II), C_{2h} (III), C_1 (IV). For the isomer I (C_{4v}) one finds the following species in Table I-11: A_1 , A_2 , B_1 , B_2 , E . This molecule has three different sets consisting of four equivalent nuclei (4H, 4C, and 4Br). All three representative nuclei lie in a plane of symmetry σ_d . Therefore $m=0$, $m_v=0$, $m_d=3$, $m_0=0$. The total number of nuclei is given by

$$N = 8m + 4m_v + 4m_d + m_0 = 0 + 0 + 4 \times 3 + 0 = 12 \text{ as it should be.}$$

Using the equations in the last column, one can determine the species of the 30 ($3N-6$) degrees of freedom (normal vibrational modes):

$$A_1 = 3m + 2m_s + 2m_d + m_o - 1 = 6 - 1 = 5$$

$$A_2 = 3m + m_s + m_d - 1 = 3 - 1 = 2$$

$$B_1 = 3m + 2m_s + m_d = 3$$

$$B_2 = 3m + m_s + 2m_d = 6$$

$$E = 6m + 3m_s + 3m_d + m_o - 2 = 9 - 2 = 7$$

$$23$$

Consequently, there are 23 normal vibrational modes: $5A_1$, $2A_2$, $3B_1$, $6B_2$ and $7E$. The 7 modes E (doubly degenerate) involve 14 degrees of freedom; therefore, there are 30 vibrational degrees of freedom. The normal translational modes are: $1A_1(T_z)$ and $1E(T_x, y)$ and the rotational modes are: $1A_2(R_z)$ and $1E(R_x, y)$. Since each doubly degenerate mode involves two degrees of freedom, there are three translational and three rotational degrees of freedom (totaling 6).

The data in Column 4 (Table I-11) show that only species A_1 and E are active in the infrared. Consequently, there are 12 vibrational modes active in the infrared: $5A_1$ and $7E$.

By a similar procedure, one determines that the isomer II (D_{2d}) has 12 modes active in the infrared: $5B_2$ and $7E$; isomer III (C_{2v}) has 15 modes ($8A_1$ and $7B_1$), and the asymmetric isomer IV has all 30 vibrations active in the infrared.

The infrared spectrum of one of the four isomers (m.p. 104°C ; Fig. I-40 a) has very few bands, suggesting structures C_{4v} or D_{2d} . Chemical reasons preclude the structure with C_{4v} symmetry. The spectrum of another isomer (Fig. I-40b) shows a larger number of bands, supporting structure C_{2v} . Nuclear magnetic resonance spectra are in agreement with these assignments [55].

j. The symmetry of dipole moments and of vibrational states. The three components M_x , M_y , M_z of the dipole moment M of the molecule, show the same behavior as the displacement vectors of the nuclei in various normal vibration modes with respect to symmetry elements. Therefore they can be

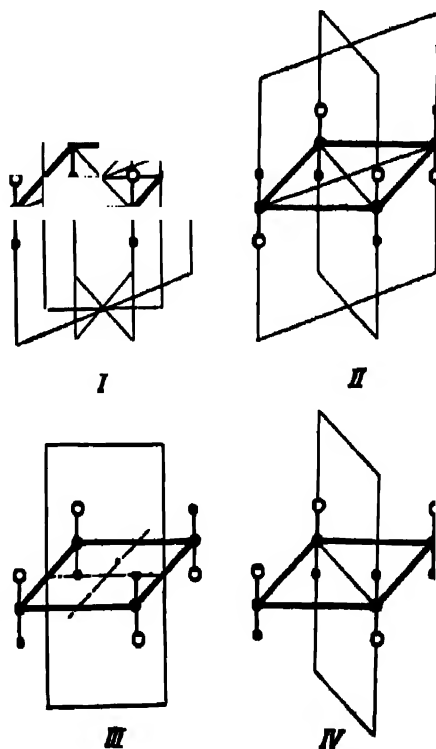


Fig. I-39 The symmetry of the four isomers of 1, 2, 3, 4-tetra-bromocyclobutane. O bromine atom; ● carbon atom; • hydrogen atom.

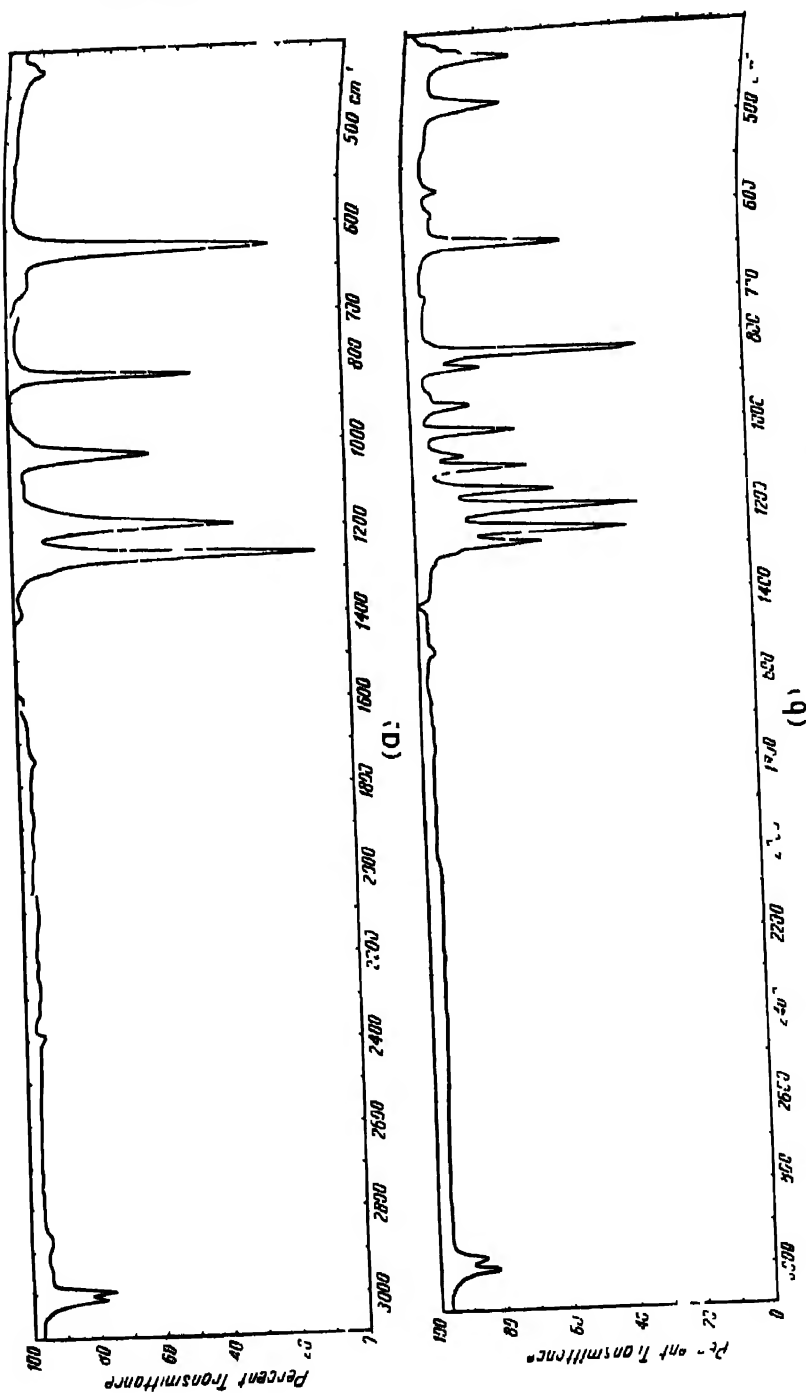


Fig 1-40 Infrared spectrum of 1, 2, 3, 4-tetrabromocyclobutane:
 (a) $\text{C}_4\text{H}_2\text{Br}_4$, m.p. 104°C ; (b) $\text{C}_4\text{H}_2\text{Br}_4$, m.p. 87°C .

characterized in the same way for each rotational or vibrational state of the molecule. Table I-12 shows symmetry types of dipole moments in the principal point groups.

Table I-12 Symmetry of dipole moments

| Point group | Species M_x M_y M_z | Point group | Species M_x M_y M_z | Point group | Species M_x M_y M_z |
|---------------------|------------------------------|----------------|------------------------------|---------------------|------------------------------|
| C_∞ | A' A' A'' | S_6 | E_{1u} E_{1u} D_u | $D_{2d} \equiv V_d$ | E E B_g |
| C_1 | A_u A_u A_u | D_3 | E E A_2 | D_{3d} | E_u E_u A_{2u} |
| C_2 | B B A | D_4 | E E A_2 | D_{4d} | E_1 E_1 D_2 |
| C_{2v} | B_1 B_2 A_1 | D_6 | E_1 E_1 A_2 | D_{2h} | E' E' A'_g |
| C_{2h} | B_u B_u A_u | C_{2v} | E E A_1 | D_{4h} | E_u E_u A_{1u} |
| $D_2 \equiv V$ | B_1 B_2 B_3 | C_{4v} | E E A_1 | D_{3h} | E'_1 E'_1 A'_2 |
| $D_{2h} \equiv V_h$ | B_{1u} B_{2u} B_{3u} | C_{3v} | E_1 L_1 A_1 | D_{6h} | E_{1u} E_{1u} A_{1u} |
| C_3 | E E A | C_{6v} | E_1 E_1 A_1 | $D_{\infty h}$ | π_u π_u Σ_g^+ |
| C_4 | E E A | $C_{\infty v}$ | τ π Σ^+ | T | F F F |
| C_6 | E E A | C_{3h} | E' E' A'' | T_d | F_2 F_2 F_2 |
| S_4 | E E A | C_{4h} | E E A | O_h | F_{1u} F_{1u} F_{1u} |
| | | C_{6h} | E_u E_u A_u | | |

Symmetry properties are also valid for rotational and vibrational states. As shown in Chapter 1, the eigenvalues of the Schrodinger equation for a given potential energy represent the energy states of the corresponding vibrations. Each eigenvalue corresponds to an eigenfunction which can be described in terms of normal coordinates. It has also been shown that these coordinates, and therefore the eigenfunctions, can be symmetric (remain unchanged) or antisymmetric (change sign) with respect to a certain symmetry operation. Thus in establishing the symmetry type of the eigenfunctions, one can determine the symmetry properties of the energy states (levels) of the molecule. The behavior of the vibrational levels is given directly by the corresponding quantum numbers; for example, for a vibration which is antisymmetric with respect to a plane of symmetry, the energy levels are symmetric or antisymmetric depending on whether the quantum number is even or odd. For a vibration which is symmetric with respect to a plane of symmetry all levels are symmetric, whether the quantum number is even or odd.

Under certain conditions (see below), a vibrational eigenfunction of a molecule with N atoms may be considered as a sum of $3N$ eigenvalues of harmonic oscillators. Therefore the total eigenfunction is the product of the $3N$ eigenfunctions of the harmonic oscillators. For an antisymmetric vibration this function can be symmetric or antisymmetric, depending on whether the sum of the vibrational quantum numbers is even or odd.

The symmetry properties of the dipole moments and vibrational levels, in addition to those of normal vibrational modes, are very important in the determination of selection rules. These rules determine, in turn, which normal

vibrational modes are active in the infrared and which energy levels may be combined, or in other words, what differences in spectral terms are possible. These rules also enable a more satisfactory picture of theoretical spectra.

k. **Energy levels and vibrational spectra of polyatomic molecules.** The vibrational frequencies of a polyatomic molecule are calculated in quantum mechanics by means of the Schrödinger equation (I-9) formulated for a system of N particles. Introducing the normal coordinates and the corresponding values of the potential energy into (I-9) the equation may be resolved into $3N$ equations corresponding to the energies of $3N$ harmonic oscillators. Of these, six (in the case of nonlinear molecules) or five (in the case of linear molecules) have frequencies equal to zero (since they are translational and rotational motions). The result one gets is the same as in classical mechanics: the vibrational motion of a polyatomic molecule is a superimposition of $3N-6$ or $3N-5$ linear harmonic oscillations. The eigenvalues (energy states) of each of the $3N$ equations are given by:

$$E_i = h\nu_i \left(\nu_i + \frac{1}{2} \right), \quad (\text{I-103})$$

where $\nu_i = 0, 1, 2, \dots$ is the vibrational quantum number, and ν' is the frequency of the oscillator. The total vibrational energy of the system is:

$$E(\nu_1, \nu_2, \nu_3, \dots) = h\nu_1' \left(\nu_1 + \frac{1}{2} \right) + h\nu_2' \left(\nu_2 + \frac{1}{2} \right) + h\nu_3' \left(\nu_3 + \frac{1}{2} \right) + \dots \quad (\text{I-104})$$

The corresponding spectral terms are

$$G(\nu_1, \nu_2, \nu_3, \dots) = \frac{E(\nu_1, \nu_2, \nu_3, \dots)}{hc} \quad (\text{I-105})$$

If one writes

$$\omega_1 = \frac{\nu_1'}{c}; \quad \omega_2 = \frac{\nu_2'}{c}; \quad \omega_3 = \frac{\nu_3'}{c}, \dots, \quad (\text{I-106})$$

one has

$$G(\nu_1, \nu_2, \nu_3, \dots) = \omega_1 \left(\nu_1 + \frac{1}{2} \right) + \omega_2 \left(\nu_2 + \frac{1}{2} \right) + \omega_3 \left(\nu_3 + \frac{1}{2} \right) + \dots \quad (\text{I-107})$$

ω_i is the classical vibration frequency in cm^{-1} . To take into account degenerate vibrations, the above equation can be written

$$G(\nu_1, \nu_2, \nu_3, \dots) = \sum \omega_i \left(\nu_i + \frac{d_i}{2} \right), \quad (\text{I-108})$$

where d_i is the degree of degeneracy (in the case of nondegenerate vibrations $d_i = 1$). The zero point energy is

$$G(0, 0, 0, \dots) = \frac{1}{2} \omega_1 + \frac{1}{2} \omega_2 + \frac{1}{2} \omega_3 + \dots \quad (\text{I-109})$$

For polyatomic molecules this energy can be fairly large. The vibrational energy is often expressed with respect to the lowest energy level (zero point energy):

$$G_0(v_1, v_2, v_3, \dots) = G(v_1, v_2, v_3, \dots) - G(0, 0, 0, \dots) = \omega_1 v_1 + \omega_2 v_2 + \omega_3 v_3 + \dots \quad (\text{I-110})$$

Figure I-41 shows a part of the energy level diagram for the simplest case of a triatomic molecule. The levels in the first series correspond to

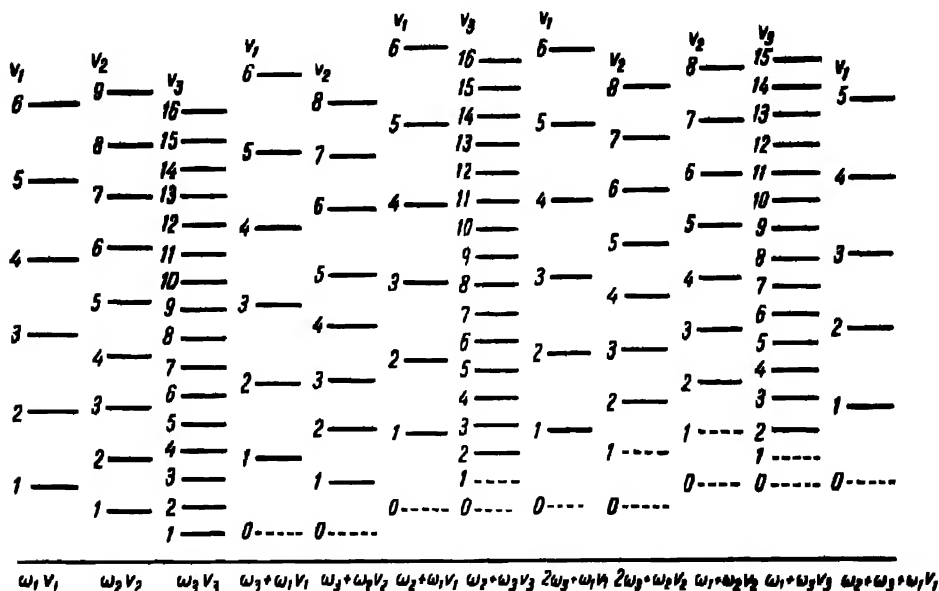


Fig. I-41 Vibrational levels of a triatomic molecule [1b].

$v_1=0, 1, 2, 3, 4, 5, 6$. For each of these values the other two quantum numbers v_2 and v_3 are equal to zero. The distance between two consecutive levels (which is constant) is 1. The levels in the second series correspond to $v_2=0, 1, 2, 3, 4, 5, 6, 7, 8, 9$. For each of these values the other two quantum numbers v_1 and v_3 are equal to zero. The distance between two consecutive levels is ω_2 . In the third series, v_3 takes values from 0 to 16 and v_1 and v_2 are equal to zero.

Obviously, the distance ω_3 between two consecutive levels is constant since in the example chosen the vibrations are considered linearly harmonic. Figure I-41 also shows energy levels of several series where, for a number of values of one quantum number, the other two quantum numbers are not equal to zero; for example, in the fourth series, v_1 takes the values 0, 1, 2, 3, 4, 5 and 6. For each of these values $v_2=1$ and $v_3=0$.

It can be seen that the energy level diagram of a polyatomic molecule is much more complicated than in a diatomic molecule even if the oscillations are harmonic.

In the interaction between matter and infrared radiations, the transitions between various levels (absorption or emission) are determined by the simultaneous change in dipole moment (this is the coupling mechanism in the resonance phenomenon*). The normal vibration modes, resulting in a simultaneous change in dipole moment, are *active* in the infrared. Vibrations which do not fulfill this condition are infrared inactive. Obviously if it does occur, the change in dipole moment has the same frequency as the vibration which generates it. For a normal vibrational mode to be infrared active, it is necessary and sufficient that at least one of the three components, M_x , M_y , M_z , of the dipole moments change. In the case of polyatomic molecules, this does not necessarily imply the existence of a permanent dipole moment, as in the case of diatomic molecules. The periodic change in dipole moment may involve only its direction or both its direction and its size.

In asymmetric molecules, any vibrational mode involves a change in dipole moment. When the symmetry of the molecule (i.e., the symmetry of the vibrations) increases, there are fewer possibilities for the dipole moment to change. Totally symmetric vibrations are not accompanied by changes in dipole moment (see example ν_1 in Fig. I-24). This does not mean that any molecule with a certain degree of symmetry must have vibrations which are inactive in the infrared. In the case of the water molecule (Fig. I-36), for example, all three normal vibration modes are accompanied by a change in dipole moment and are infrared active. The data in Table I-11 concerning the activity in the infrared of various vibrational modes are based on the comparison of their behavior with respect to the corresponding symmetry operations and changes in dipole moment. This comparison has shown that a vibration is infrared active only if it behaves with respect to all possible symmetry operations for the given molecule the same way as at least one of the components of the dipole moment. In other words, in order to determine whether a vibration of a given species is active in the infrared, it is sufficient to know whether at least one of the components of the dipole moment belongs to the same species; for example, the molecule $C_4H_4Br_4$ (page 86) belonging to the point group C_{4v} can have five species of normal vibrations: A_1 , A_2 , B_1 , B_2 and E . The data in Table I-12 show that the components of the dipole moment in this point group belong to the species $E(M_x, M_y)$ and $A_1(M_z)$. Therefore only the vibration modes of species A_1 and E are active in the infrared (see Table I-11, point group C_{4v}).

A special mention has to be made with regard to vibrations in point groups having a center of symmetry, for example C_{2h} (see Table I-11). All

* The phenomenon is comparable to the energy exchange between a vibrating tuning fork and an identical tuning fork which is not vibrating. The second tuning fork also starts to vibrate. The resonance condition (equal frequencies) is obeyed. The energy exchange is possibly due to the coupling mechanism of the air.

modes active in the infrared (antisymmetric with respect to i) are inactive in Raman and all modes active in Raman are inactive in the infrared. This is the *rule of mutual exclusion*. The validity of this rule in the case of one of the two dimers of cyclobutadiene (Fig. I-42) was one of the main arguments in assigning it the *anti* configuration. The rule of mutual exclusion does not imply that all transitions that are forbidden in Raman occur in the infrared and vice versa. Some transitions are forbidden in both.

Thus infrared spectra of any molecule have a number of fundamental bands whose frequencies are those obtained by the solution of the secular equation (I-101). For reasons shown above, not all fundamental frequencies occur in the infrared spectrum. The theoretical spectrum of a molecule may be obtained from (I-107) by applying the selection rules of the quantum theory which allow only transitions where

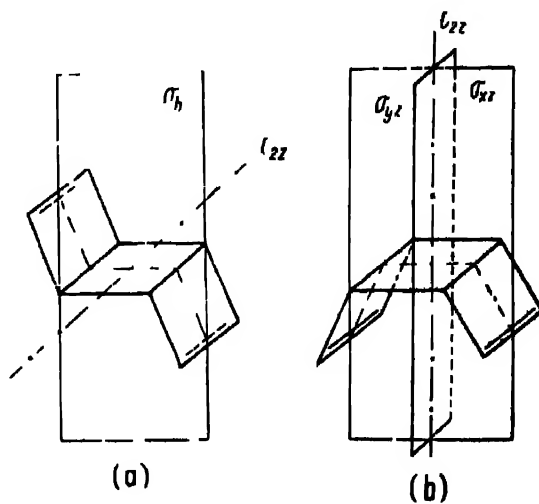


Fig. I-42
 (a) σ_h (b) σ_{vz} in cyclobutadiene $[1200\ 0]$
 octadecahedron - 3, 7

$$\Delta v_i = \pm 1 \quad (\text{I-111})$$

In the approximation in (I-103) to (I-110), one considers that each harmonic oscillator is independent. This means that the wave number of each band is

$$\nu = \omega_i \quad (\text{I-112})$$

The selection rules obtained by means of quantum mechanics show that the symmetry properties of the dipole moments are indeed essential in determining the activity in the infrared of the normal (fundamental) vibrational modes.

1. Anharmonicity and interaction of vibrations. Overtones, combination bands. Since vibrations are anharmonic, infrared spectra of polyatomic molecules show overtones, $2\nu_i$, $3\nu_i$, ..., the same as those of diatomic molecules (see page 41). Combinations $\nu_i + \nu_j$, $\nu_i - \nu_k$, $2\nu_k - \nu_k$, $2\nu_k - \nu_i$, $\nu_k - \nu_i - \nu_i$... are also possible. The intensity of overtone and combination bands is generally much lower than that of fundamental bands. Whenever possible, the identification of these bands is important in the vibrational analysis of a molecule.

Fermi resonance. It may happen that in a polyatomic molecule two different vibrational levels (or combinations of vibrations) may have nearly the same energy. In other words, they may be *accidentally degenerate*. If these

vibrations belong to the same species, a mutual perturbation of the energy levels may occur, resulting in a shift of one of them toward lower energies and of the other toward higher energies. The phenomenon may be accompanied by a substantial increase in intensity of the respective bands and is called *Fermi resonance* because Fermi was the first to notice it in the carbon dioxide molecule.

The infrared spectrum of carbon dioxide shows two very strong bands, at 667.3 and 2349.3 cm^{-1} assigned to the *fundamentals* ν_2 (species Π_u) and ν_3 (species Σ_g^+), respectively.

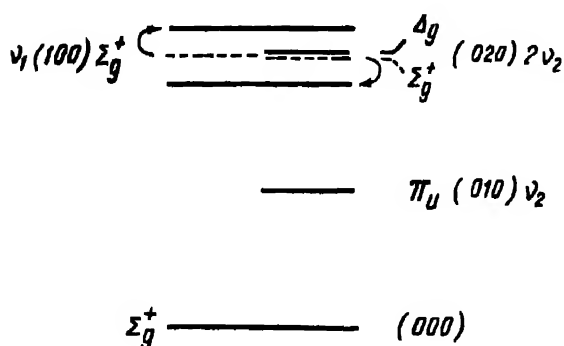


Fig. I-43 Fermi resonance in the carbon dioxide molecule. The levels which shift as a result of the perturbation are shown by dotted lines.

the overtone $2\nu_2$ ($\nu_1=0$, $\nu_2=2$, $\nu_3=0$), a Fermi resonance takes place, resulting in a shift of the first level toward a higher energy and of the second level toward a lower energy (Fig. I-43). The intensity ratio of the two bands is 1:0.59. Each level occurring as a result of the interaction is a combination of the two levels involved in resonance. Actually, the overtone $2\nu_2$ consists of two sublevels, Σ_g^+ and Δ_g . Only the first one can be perturbed, since it has the same species as the level of the fundamental ν_1 . The transition between the level of the fundamental and the level Δ_g is also allowed in Raman. However, since it is not perturbed, it has the very low intensity of an ordinary overtone and is hard to detect in the spectrum.

As a consequence of the resonance $\nu_1-2\nu_2$, there are other perturbations between higher levels (overtones or combinations).

Several examples of Fermi resonance are given in the second part of this book.

m. Characteristic group frequencies. By comparing spectra of a large number of organic compounds, it has been observed that the presence of certain types of bonds (e.g., O—H, N—H, $\equiv\text{C—H}$, $>\text{C—H}$, $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$, etc.) in various molecules may be correlated with the constant occurrence of absorption bands in the infrared whose positions are only slightly altered in going from one compound to another. Thus one can assume that the atomic group vibrates independently (has its own frequency). These frequencies are called

characteristic group frequencies. This notion is in contradiction with the theory which states that an *infrared absorption* is due to a *normal active vibration* involving the vibrations of all atoms of a molecule. However, the contradiction is only apparent. A chemical bond, for example the C—H bond, has practically the same electronic structure, i.e., the same force constant in various molecules, provided that the molecular structure in the vicinity of the bond is similar. Assuming that the influence of the rest of the molecule is very small (see below), one may consider that the normal vibration is localized in the respective bond and is determined by the force constant and the mass of the atoms according to Hooke's law:

$$\nu = \frac{1}{2\pi r} \left(\frac{k}{\mu} \right)^{1/2} \quad (\text{I-113})$$

where ν is the wave number, k is the force constant of the bond, and μ the reduced mass of two atoms; for example, in the case of a simple bond, the value of k is of the order $5 \cdot 10^5$ dyne/cm. If one assigns this value to the force constant of the C—H bond and introduces the atomic masses of carbon and hydrogen ($19.8 \cdot 10^{-24}$ g and $1.64 \cdot 10^{-24}$ g, respectively), (I-113) gives for the frequency of the C—H bond the value 3040 cm^{-1} , comparable with experimental values (2850 – 2960 cm^{-1}) for C_2H_2 , CH_4 , and CH_3 groups in alkanes. The differences arise from the fact that vibrations of each group are more or less influenced by the structure of the molecule in the immediate neighborhood of the bond. If the frequencies were absolutely free from any influence, the infrared spectrum would tell us only whether a certain atomic group is or is not present in a molecule. However, since the force constant of a bond changes with its electronic structure, the resulting characteristic shifts in vibrational frequency enable us to gather more information with regard to the respective bond.

Frequency shifts generally result from *mechanical or electronic effects*. Mechanical effects arise from alterations in masses or from coupling of vibrations of adjacent bonds. They do not affect the force constant of the bond. Electronic interactions may affect the form and frequency of vibrations only by altering the individual force constants as a result of alterations in electron density due to *conjugative or inductive effects*.

These effects are transmitted through chemical bonds. In some instances *steric effects* may occur, resulting in either the *hindrance of electronic effects* (e.g., hindrance of conjugation in 2, 3, 5, 6-tetramethylacetophenone, where the CO group is forced from the plane of the aromatic ring by the substituents) or in polar effects transmitted through space (e.g. in α -bromocyclohexanone with an equatorial halogen, the frequency of the carbonyl group is 20 cm^{-1} higher than in unsubstituted ketones; whereas in the compound with an *axial* halogen the frequency shift is no larger than 2 – 3 cm^{-1} . The increase in frequency when the C-Hal and C=O bonds have a parallel orientation is attributed to a *dipole-dipole interaction* transmitted through space, or in other words, to a *field effect*). It should be pointed out that electric effects some-

times result in a substantial increase in intensity of the bands arising from the affected vibrations.

Only in rare instances is it impossible to distinguish between mechanical and electronic interactions. One such case is hydrogen bonding, which seems to involve a combination of both interactions. Actually, hydrogen bonds have to be considered separately.

The simple example of the HCN molecule enables us to define clearly the notions of *group frequency*, *stretching vibration*, and *deformation vibration*. We recall that a normal vibration has to proceed in such a way that it does

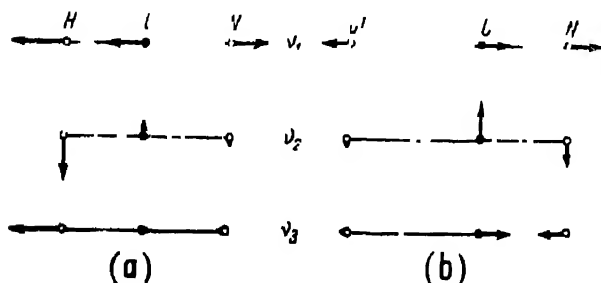


Fig. 1-44 Normal vibration modes of molecules
(a) HCN and (b) ClCN.

not alter the position of the center of gravity of the molecule. The direction and size of the vectors for a given frequency are determined by the mass of the atoms, the force constants, and the bond angles. Obviously, the lightest atoms have the largest amplitudes. Thus the ν_3 mode (Fig. 1-44a) is character-

ized by the almost exclusive vibration of the hydrogen atom with respect to the CN group, which is practically motionless. The frequency of such a vibration is given approximately by (I-113) since it is characterized by the presence of a single restoring force. The mode ν_3 is a typical example of *group frequency*. It is to be expected that all compounds with a H—C—X group (where X is the heavier, mono- or polyatomic part of the molecule) will have a normal vibration mode characterized by the oscillation of the hydrogen atom linked to the rest of the molecule through a carbon atom. Such a vibration mode is called, according to Mecke, a *valence vibration* since it can only take place in the valence line of the particular bond. If one now considers the modes ν_1 (2089 cm^{-1}) in the molecule HCN (Fig. 1-44a) and ν_3 (2200 cm^{-1}) in the molecule ClCN (Fig. 1-44b), one can easily see that one is dealing with CN *valence vibrations*, since in the first case the atoms C and H are displaced together in opposite direction with respect to the displacement of atom N, whereas in the second case the atom Cl is practically motionless. Another name for *valence vibration* is *bond-stretching* or simply *stretching vibration*. Its symbol is the letter ν followed by the corresponding group (e.g., νCII).

Vibrations ν_2 in Fig. 1-41 a and b are characterized by the alteration of bond angles. For this reason they were called *deformation vibrations*. Their symbol is δ , (e.g., δCII). If the vibration of the dipole moment is perpendicular to a main plane (e.g., the plane of the molecule) the deformation vibration is called γ ; if it is parallel to this plane, the notation δ is maintained.

In many instances the concept of group frequencies is meaningless. This must be kept in mind in order to avoid erroneous conclusions. The main reason is *coupling* of vibrations arising from adjacent bonds. For example, if the stretching vibrations C—H and C≡N in HCN were isolated normal harmonic vibrations, they should obey Hooke's law (I-113). On substitution of hydrogen with deuterium the frequency of the CD bond should be smaller than that of the CH bond (ratio $\nu_{\text{CH}}/\nu_{\text{CD}}=1.41$) and should occur at 2430 cm^{-1} while the frequency of the C≡N vibration should remain unchanged (2089 cm^{-1}). Actually in DCN the corresponding frequencies are 2629 and 1906 cm^{-1} . This

| Vibration | Wave number | Species | Nature of vibration | Activity | |
|------------|-------------|--------------|---|----------|----|
| | | | | R | IR |
| ν_1 | 3374 | Σ_g^+ | ν_{CH} sym | a | ia |
| ν_2 | 1974 | Σ_g | $\nu_{\text{C}\equiv\text{C}}$ | a | ia |
| ν_3 | 3287 | Σ_u^+ | ν_{CH} asym | ia | a |
| ν_{4a} | 612 | Π_g | $\delta_{\text{C}\equiv\text{C}}$ -H sym | a | ia |
| ν_{4b} | | | | | |
| ν_{5a} | 729 | Π_u | $\delta_{\text{C}\equiv\text{C}}$ -H asym | ia | a |
| ν_{5b} | | | | | |

Fig. I-15 Normal vibration modes of acetylene

means that vibration ν_3 is affected not only by the mass of the atom H, and that vibration ν_1 is not totally independent of the mass of H. To some extent the two vibrations are *coupled*. The coupling process can be better described in the case of acetylene (see Fig. I-45). The mode ν_1 is a symmetric ν_{CH} vibration, the mode ν_3 is an asymmetric ν_{CH} vibration, and the mode ν_2 is the C≡C stretching vibration. The frequencies of these vibrations are shown in Table I-13 along with the corresponding frequencies in C_2D_2 . It can be seen that in the case of the ν_{CH} asymmetric vibration, the isotope effect is close to that predicted by theory for the harmonic oscillator. In the case of the symmetric vibration the effect is much smaller;

Table I-13 Frequencies of stretching vibrations in C_2H_2 and C_2D_2

| Vibration | C_2H_2 cm^{-1} | C_2D_2 cm^{-1} | Ratio * $\nu_{\text{CH}}/\nu_{\text{CD}}$ | Species |
|--------------------------------|--|--|--|--------------|
| ν_{CH} sym | 3374 | 2701 | 1.249 | Σ_g^+ |
| ν_{CH} asym | 3287 | 2427 | 1.354 | Σ_u^+ |
| $\nu_{\text{C}\equiv\text{C}}$ | 1974 | 1752 | 1.120 | Σ_g^+ |

* Theoretical value 1.41.

the $\nu\text{C}\equiv\text{C}$ vibration is also affected. This shows that the modes $\nu\text{C}\equiv\text{C}$ and νCH sym are coupled whereas νCH asym is almost totally independent. This selection in the coupling of vibrations is because only vibrations belonging to the same symmetry species can be coupled. In the given example, the coupled vibrations (ν_1 and ν_2) have both Σ_g^+ symmetry. This shows that group frequencies must be interpreted with caution.

Generally speaking, there are two categories of group frequencies: frequencies arising from the vibration of a very small atom (H or D) which are only slightly affected by the structure, and vibrations of the rest of the molecule. The highest frequencies belong to X—H bonds since the force constant of these bonds does not differ much from that of other simple covalent bonds (X—Y) whereas the reduced mass of the atoms X and H is considerably smaller. In the infrared, the highest fundamental frequency (3950 cm^{-1}) arises from the H—F bond (the H—H bond frequency can be observed only in Raman, at 4400 cm^{-1}). The frequency decreases with increasing atomic weight of the halogen. HCl absorbs at 2900 cm^{-1} , HBr at 2650 cm^{-1} and HI at 2309 cm^{-1} .

In X—D bonds the isotopic shift is entirely due to the mass effect since the force constants (electronic structures) of X—H and X—D bonds are practically equal (see page 54). Equations 1.113 and 1.22 give

$$\frac{\nu_{\text{X-D}}}{\nu_{\text{X-H}}} = \left(\frac{2+m}{2+2m} \right)^{1/2} \quad (1-114)$$

where m is the atomic weight of X. For O—D, N—D, and C—D, the calculated shifts are $\sqrt{1.89}$, $\sqrt{1.87}$, and $\sqrt{1.86}$, respectively (ca. $\sqrt{2}$). As shown, the shifts observed on substitution with deuterium are smaller than expected.

In the case of X—Y bonds, where both X and Y are heavy atoms, the increase of the reduced mass results in a substantial decrease in frequency. C—C, C—O, and C—N bonds absorb in the medium frequency region, contributing to the complex pattern of spectra of organic compounds between 700 and 1500 cm^{-1} .

The force constant of X=Y double bonds is approximately twice as large as that of simple covalent bonds. Consequently, frequencies of the C=C, C=O, C=N, and N=O stretching vibrations lie in the range 1500 – 2000 cm^{-1} . The electronic structure of X=Y bonds is very sensitive to inductive and conjugative effects. As shown in the second part of this book, small shifts in characteristic frequencies arising from these groups can be interpreted semiquantitatively as alterations in the double bond character.

In X \equiv Y bonds the force constant is approximately three times as large as in simple X—Y bonds. This results in an increase in frequency above 2000 cm^{-1} . C \equiv C and C \equiv N absorb between 2000 and 2300 cm^{-1} . The coupling of bonds with large force constants is much smaller than in the case of other bonds.

Having much smaller force constants, deformation modes X—H and X—Y give rise to much lower frequencies than stretching vibrations. In

general, δ CH bands occur in the region $650\text{--}1650\text{ cm}^{-1}$, overlapping with X—Y stretching mode bands. In many instances resonance phenomena occur between ν X—Y and δ X—H vibrations with practically coincident frequencies. This complicates even more the interpretation of infrared spectra in the respective region, but at the same time the pattern that arises is characteristic for each compound. O—H deformation vibrations give rise to frequencies between 1200 and 1400 cm^{-1} . NH deformations occur above 1500 cm^{-1} .

Figure I-46 shows the approximate limits of the principal group frequencies. X—Y deformations give rise to very low frequencies (below 500 cm^{-1}).

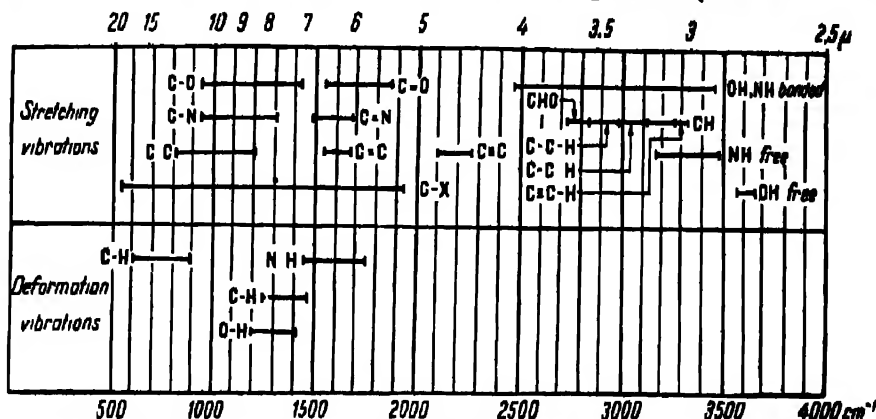


Fig. I-46 Approximate limits of the principal characteristic group frequencies.

Another type of characteristic frequencies arises from *skeletal vibrations*; for example, in benzene all six carbon atoms are involved in vibrational modes which are not localized in a certain bond. Ring substituents do not alter substantially the skeletal frequencies. Isopropyl, isobutyl, and tert-butyl groups also have characteristic frequencies.

More details on characteristic frequencies of the principal classes of organic compounds discussed in this book are shown in Appendix I. It should be pointed out that the conventional assignment of vibrations to two categories — *stretching* and *deformation* — although very useful in the description of vibration spectra of organic compounds, is not always adequate. In certain instances the rigorous differentiation between stretching and deformation vibrations is precluded by coupling effects with adjacent atoms. This is generally the case with internal groups, which in contrast to terminal groups cannot be treated strictly in terms of the classification *stretching-deformation*.

4. Rotation-vibration spectra of polyatomic molecules

In polyatomic molecules (with large moments of inertia), the separations of rotational levels are too small to be resolved. When they can be observed, the rotation-vibration bands of these molecules actually represent the fine structure envelope of branches P, Q, and R.

Branches P and R correspond to various values taken by the vibrational quantum number when the rotational quantum number increases or decreases (see rotation-vibration spectra of diatomic molecules). Branch Q corresponds to variations of the vibrational quantum number unaccompanied by changes in the rotational quantum number. The form and intensity of branches P , Q , and R are determined by selection rules based on the symmetry of the vibrations and on the ratio of the moments of inertia about the three principal axes of the molecule (A , B , C). In other words, the contour of rotation-vibration bands is closely related to the symmetry of the molecule.

In contrast to diatomic molecules, linear polyatomic molecules ($I_A = 0$, $I_B = I_C$) may have deformation vibrations in addition to stretching vibrations. Stretching vibrations with a transition moment in line with the axis of symmetry of the molecule are called *parallel vibrations* and the corresponding absorption bands are called *parallel bands*. These bands are characterized by the presence of P and R branches and the absence of the Q branch since linear polyatomic molecules (akin to heteronuclear diatomic molecules) do not have odd electrons that would give rise to an angular momentum about the axis (see band ν_3 in the spectrum of carbon dioxide, Fig. 1-17a). Conversely, *perpendicular bands* (corresponding to deformation vibrations with a transition moment perpendicular to the axis of symmetry of the molecule) show a Q branch associated with the angular momentum arising from the motion of the nuclei perpendicular to the axis of symmetry (see band ν_2 Fig. 1-17b).

The methane molecule is an example of a spheric top ($I_A = I_B = I_C$). The only infrared active species of vibrations (see Table 1.11, point group T_d) is the species F_2 with stretching vibrations ν_3 (3020.3 cm^{-1}) and deformation vibration ν_4 (1306.2 cm^{-1}). The rotation-vibration bands of the spheric top have the same structure as the perpendicular bands in linear molecules. The rotation-vibration band ν_3 in methane is shown in Fig. 1-17c).

Benzene and methyl chloride molecules are examples of *symmetric tops* ($I_A \neq I_B = I_C$). If the two equal moments are smaller than the third one, the molecule is called *prolate symmetric top*. This is the case of benzene. If the two equal moments are larger than the third one, the molecule is called an *oblate top*. This is the case of methyl chloride.

When the change of the dipole moment takes place along the *principal axis of symmetry*, the vibration and the corresponding absorption band are *parallel*. When the moment is oriented *perpendicular* to this axis, the vibration and the corresponding absorption band are *perpendicular*.

In the case of the symmetric top *hybrid bands* are possible, having on one hand a *parallel character* and on the other hand a *perpendicular character*. Depending on the selection rules valid in these instances, a number of *subbands* may arise, called P_P , P_Q , P_R , Q_P , Q_Q , Q_R , R_P , R_Q and R_R . When they can be obtained, the envelopes of these bands are complicated. The parallel band of a prolate symmetric top is roughly similar to the perpendicular band of a linear molecule. In perpendicular bands the unresolved series

of lines Q_P , Q_Q and Q_R , may appear as stronger bands than the adjacent lines.

Most molecules are best represented by the *asymmetric top* ($I_A < I_B < I_C$). The observed bands are of type A, B, or C, depending on the orientation of the transition moment which may be in line with the axis of the smallest

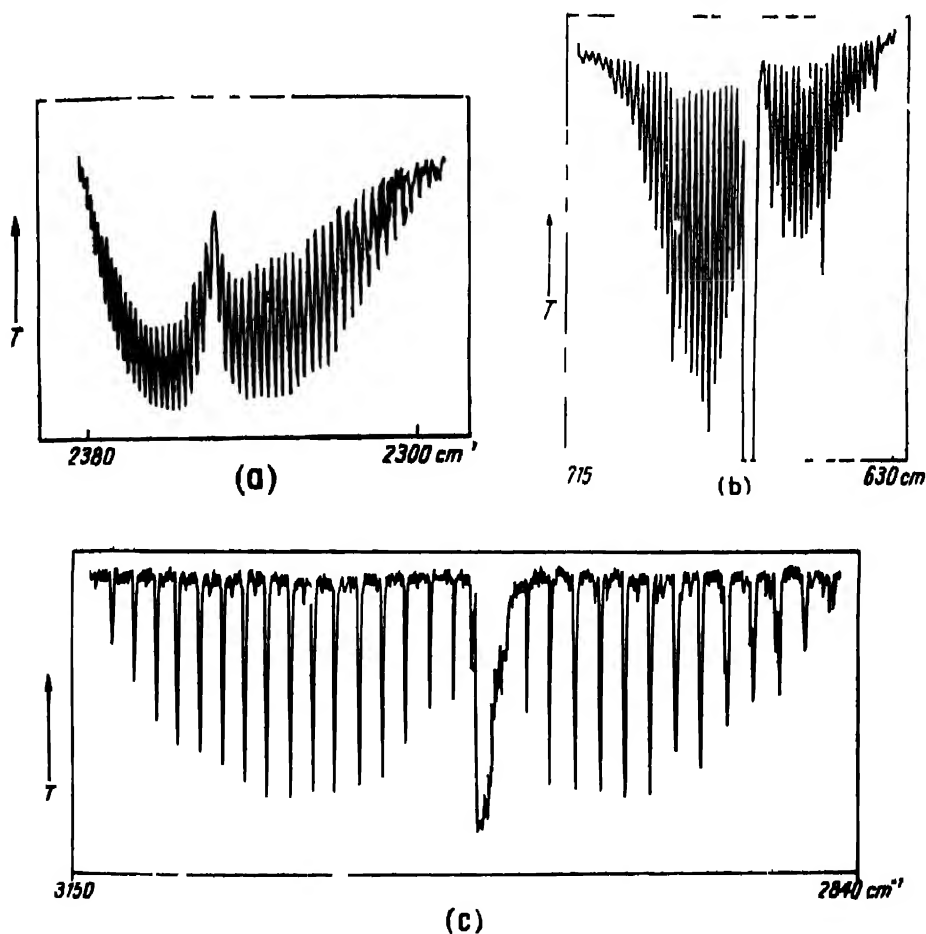


Fig. 17 Rotation-vibration spectra

(a) parallel band ν_2 in the spectrum of carbon dioxide, (b) perpendicular band ν_2 in the spectrum of carbon dioxide, (c) ν_3 band in the spectrum of methane

medium, or largest moment of inertia, respectively. *Hybrid* bands are more likely to appear in this case than in any other type of molecule.

Generally speaking, it is not the scope of organic chemistry to interpret rotational-vibrational fine structures. However, the analysis of such bands in small molecules was very important in the determination of some characteristic group frequencies.

5. Molecular vibrations in liquids and solids

Infrared spectra of compounds recorded in the liquid or solid state are very different from those recorded in the gaseous state. This is primarily because of collisions and interactions of molecules which are the stronger the smaller the distance between the molecules. The first noticeable effect is the disappearance of the rotational structure of vibration bands; for example, in the case of hydrogen chloride (Fig. 1-48), the increase in pressure results in a progressive superimposition of lines belonging to the fine structure. At 45 atm., one can observe only the contour of branches *P* and *R*, and beyond the critical point the two branches are very difficult to observe. In the liquid phase at -45°C , only one band is noticeable. Its strongest absorption occurs at a slightly lower frequency than the origin of the rotation-vibration band (ν_0) of the gas at normal pressure. This shows that the HCl molecule in the liquid state does not have quantized rotation states. With very few exceptions, (e.g. H_2), this observation holds for all molecules in the liquid state. In some instances, a rotational structure of some vibrational

bands has been observed in spectra of solutions (e.g., ammonia in water and water in carbon tetrachloride). In the solid state (again with the exception of hydrogen), the quantized rotation of molecules could not be demonstrated spectroscopically.

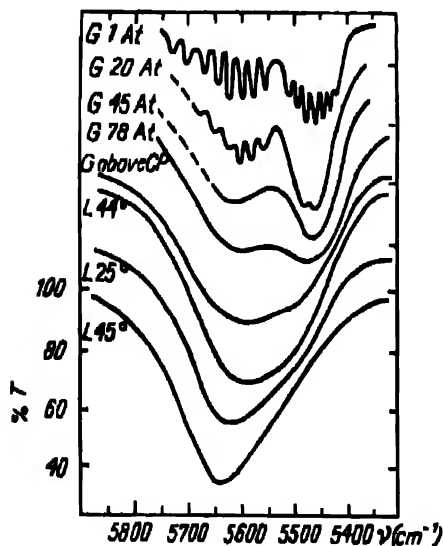


Fig. 1-48 The band of the first overtone of hydrogen chloride in gaseous state (*G*) and liquid state (*L*) at various pressures and temperatures.

Vibrations of molecules can take place both in the liquid and solid states. Two kinds of changes appear in the vibration of molecules in going from the vapor phase to liquid or solid state: (a) frequency shifts and (b) the occurrence of new bands. Frequency shifts are generally small (below 5 %) between vapors and liquids. Sometimes they may become larger in solution. A characteristic example for the occurrence of new bands is the formation of dimers and polymers by *hydrogen bonding*. In the case of conformational isomers (in molecules with internal rotation), infrared spectra sometimes become

simpler when recorded in the solid state in which one of the conformations is energetically favored. As shown above, vibrational spectra of free molecules in the gaseous state are strictly dependent on molecular symmetry. The same criteria may be applied to the interpretation of spectra recorded in the crystalline state. In this case the number of molecules in an elementary cell

plays the main role. Nuclear motions in crystals may occur either within the *vibrations of the lattice* (where the molecules are considered rigid) or within the *vibrations of the molecules* (corresponding to vibrations of free molecules, but affected by the intermolecular forces of the elementary cell). The difference between the spectrum of a molecule in the crystalline state and that of a free molecule is greater, the higher the polarity of the molecule.

While vibrational spectra of gases and crystals can be interpreted by means of well-established (though complicated) criteria, vibrational spectra of molecules in the liquid state cannot be completely analyzed. This is primarily because selection rules are no longer rigorously valid since, to a certain extent, the molecule loses its symmetry properties as a result of intermolecular interactions.

6. Photometric Definitions, Units, and Nomenclature. Absorption Laws*

When a parallel beam of monochromatic light of wavenumber $\tilde{\nu}$ passes through a sample in a cell of thickness l (Fig. I-49), the radiant intensity I_1 of the incident beam will decrease to a final value I_0 as a result of reflections at interfaces between the various media, diffusion phenomena, absorption by the windows, and absorption by the analyzed sample. The ratio of transmitted to incident radiant intensity (I_0/I_1) is called *transmittance* $\dagger(\tau)$. If only absorption by the sample is considered, the ratio I/I_0 is called *internal transmittance* $\dagger(T)$. The ratio of absorbed to incident radiant intensity, $(I_0 - I)/I_0$, is called *absorptance* $\dagger(\alpha)$. In most photometric measurements, we consider *per cent transmittance*: $\% T = 100 T = 100(I/I_0)$ or (less commonly) *per cent absorptance*: $\% \alpha = 100(I_0 - I)/I_0$.

a. **The Lambert-Bouguer Law.** Lambert and Bouguer have shown that absorption of monochromatic light by a homogeneous, isotropic sample depends on the radiation wavelength and the nature and thickness of the sample. Loss of radiant intensity after passing through a layer of infinitely small thickness dl is proportional to the radiant intensity of the incident beam and the thickness dl of the layer:

$$-dI_0 = bI_0 dl. \quad (I-115)$$

* The terms marked with a dagger, and their associated symbols are recommended by the International Union of Pure and Applied Chemistry and are discussed in the "Manual of Symbols and Terminology for Physicochemical Quantities and Units" (*Pure and Applied Chemistry*, Vol. 21, No. 1 (1970)). Symbolism and terminology in this field have long been confused and practice has differed in Europe and North America. The new IUPAC recommendations attempt to achieve a wider conformity extending to contiguous fields, of concern to the Commission on Illumination and International Electrochemical Commission, as well as to spectroscopists.

IUPAC also recommends that ν be used for frequency (hertz) and $\tilde{\nu}$ for wavenumber (cm^{-1}). It is, however, a common practice to use ν for wavenumber where no ambiguity with frequency is to be anticipated; this is true for most applications of infrared spectrophotometry to organic chemistry and this practice will be followed in this text, apart from this section.

The proportionality constant b , called the *Napierian absorption coefficient*, ϵ^N is a characteristic property of the sample at a given wavenumber and is independent of sample size. Integration of (I-115) between the path length zero (when radiant intensity is I_0) and l (when radiant intensity is I) gives

$$\int_{I_0}^I dI_0/I_0 = -b \int_0^l dl \quad (\text{I-116})$$

and

$$\ln I/I_0 = -\ln I_0/I = -\ln I/T = -bl = -B, \quad (\text{I-117})$$

where B is the *Napierian absorbance*. The *Napierian absorption coefficient* $b = B/l$.

Equation (I-117) may be written in its exponential form:

$$I = I_0 e^{-bl}. \quad (\text{I-118})$$

Using decadic logarithms gives

$$I = I_0 10^{-al} \quad (\text{I-119})$$

where a is the (*decadic*) *absorption coefficient*†* ($a = 0.4373b$; $b = 2.303a$). Equations (I-118) and (I-119) show that the *Napierian absorption coefficient* b and the (*decadic*) *absorption coefficient* a are the reciprocal of path length l when radiant intensity decreases to $1/e$ (ca. 37%) and $1/10$ respectively, of the initial value I_0 . The exponent al in Equation (I-119) is the (*decadic*) *absorbance*† (A)², this quantity is known as *optical density* (OD) or *extinction* (E)**.

$$A = \text{OD} = E = al = \log_{10}(I_0/I) = \log_{10}(1/T) \quad (\text{I-120})$$

b. **Beer's law.** In 1852 Beer showed that absorption depends on the number

of molecules interacting with the electromagnetic radiation. Thus, the absorption coefficients b and a completely characterize the absorption properties of a material in the solid or liquid state (where the number

* This quantity is also known in spectrochemistry as *absorptivity* or *extinction coefficient*.

** The term *extinction* is now internationally recommended for diffusion of radiation and not for absorption. The term *absorbance* is increasingly being used and tends to become a standard International name since, on one hand, its root gives a direct characterization of the main process taking place and, on the other hand, its suffix conforms to a widely-used convention where *ance* expresses a property of a substance or an instrument (e.g., inductance, reluctance, impedance, etc.). However, throughout this book we shall continue to use the term *molar extinction coefficient* for the quantity ϵ .

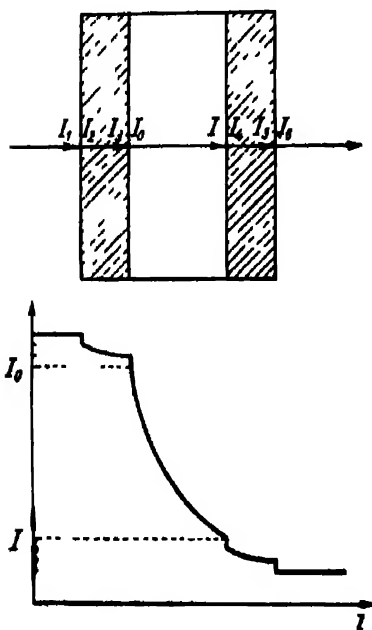


Fig. I-40 Loss of radiant intensity of a monochromatic beam on passing through an absorption cell with a path length l .

of molecules is constant) but not those of solutions, mixtures, or gases (where the number of molecules in a given volume may vary as a function of concentration or relative pressure). In the latter cases, establishment of a relationship between concentration c of the analyzed substance and the corresponding absorption is necessary. Since under the previously described conditions (monochromatic radiation, normal incidence, homogeneous sample), the number of molecules responsible for absorption is directly proportional to the concentration (or pressure) of the substance, the following relations can be written

$$a = \epsilon c \quad (I-121)$$

$$b = k c l \quad (I-122)$$

These two equations are known as Beer's law. ϵ is the *molar (decadic) absorption coefficient***

$$\epsilon = A / c l \quad (I-121a)$$

k is the *molar Napierian absorption coefficient*

$$k = B / c l \quad (I-122a)$$

where concentration c is expressed in *mole per liter*** and path length l is expressed in cm. The dimensions of ϵ are $l \text{ mole}^{-1} \text{ cm}^{-1}$. For a given wave-number, the molar absorption coefficient*** is a characteristic constant of the substance, and is independent of the concentration.

Combining the Lambert-Bouguer law with Beer's law, we obtain a single expression for both laws known as the Lambert-Beer law****.

$$A = \log_{10}(I_0 / I) = \epsilon c l \quad (I-123)$$

Beer's law is not universally applicable. Generally speaking, it is applicable to very dilute solutions. An increase in concentration may result in various molecular associations (solute-solute and solute-solvent). This makes ϵ concentration dependent. Deviations from Beer's law also occur because the incident beam is not rigorously monochromatic. This is due on one hand to scattered radiation and on the other, to the finite spectral slit width. For this reason the degree of accuracy in measurements of absorption coefficient also depends on the slit width. The absorption coefficient is also temperature dependent.

* The term *molar absorptivity* is widely used as an alternate to molar absorption coefficient, but it must be noted that in the IUPAC system the term *absorptivity* has been accepted internationally to mean absorbance per unit length (see footnote on page 107).

** The liter is to be regarded as a trivial name for dm^3 . Prior to 1961 the liter was defined as $1.000\,028 \text{ dm}^3$, but was redefined in that year by the Conférence Générale des Poids et Mesures as 1.0 dm^3 exactly.

*** This constant is also called *specific absorbance* since its value is that of absorbance when both concentration and path length are unity. Other names are *specific absorption*, *absorbance index*, *Bunsen coefficient*.

**** Actually, the Lambert-Beer law (I-123) is a result of contributions made by Bouguer, Lambert, Bunsen, Roscoe and Beer. However, when spectroscopy is applied to chemistry, we are primarily concerned with the dependence of absorption on concentration. For this reason the general tendency is to call the law simply Beer's law.

7. Presentation of infrared Spectra

The record of the spectral characteristics of a substance as a function of frequency or wavelength of the interacting radiation is generally known as a *spectrum*. The nature of the measurements and the region in which these measurements are performed are defined in a specific way. For example, a spectrum obtained by measuring the emission of a substance at wavelengths between 400 and 760 nm is known as the *visible emission spectrum* of the substance. The spectrum obtained by measuring the absorption of a substance in the ultraviolet region is called the *ultraviolet absorption spectrum*. *Reflection spectra* can be similarly defined. When molecular spectroscopy is applied to organic chemistry, it is more general to measure *absorption*, and the results of these measurements are commonly called *ultraviolet, visible, or infrared spectra*.

Brief descriptions of the various ways of presenting infrared spectra (see Fig. I-50) are given.

The abscissa may represent wavelength λ , frequency ν , or wavenumber $\tilde{\nu}$. The wavelength is measured in micrometers* (μm). The frequency unit is the *hertz* (Hz) and the wavenumber unit is the *reciprocal centimeter* (cm^{-1}).

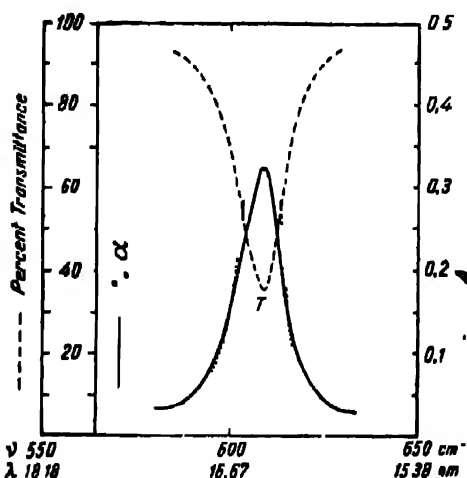


Fig. I-50 Presentation of an absorption band with various scales on the abscissa and ordinate.

The ordinate may represent *per cent transmittance* ($\%T$), *per cent absorbance* ($\%a$), *absorbance* (A), *molar absorption coefficient* (ϵ), or $\log_{10} \epsilon$.

Historical factors have played a significant role in establishing the form in which infrared spectra are commonly presented. With the early prism spectrometers it was both convenient and rational to display the spectrum on an abscissal scale linear in wavelength; it was also natural that, following Cartesian conventions, the wavelength scale should increase from left to right (Fig. I-51a). Since 1940 both linear wavelength and linear wavenumber scales have been used, with the wavenumber scale gradually gaining precedence

over the wavelength scale. There are several reasons for this. The spectrum plotted linearly in wavelength exhibits a progressive broadening of the bands towards the long wavelength end, whereas on the wavenumber scale this form of distortion does not occur (cf. Figs. I-51a, I-51b). The wavenumber scale, however, does crowd the spectrum at the low wavenumber

* The micrometer (μm) is identical to the micron (μ) and the latter term is still more widely used in the literature. This terminology is expected to change to achieve more general accord with the Internationale Système d'Unités (SI).

end, but this can be corrected by a change in the scale factor (usually at 2000 cm^{-1}) (Figs. I-52 and I-53). Another reason favoring the use of wavenumber is the linearity between wavenumber and energy through the fundamental relationship $E=h\nu$, where h is Planck's constant and c is the velocity of light. Finally, there is the correlation between the *absolute wavenumber* position of an infrared absorption band and the *wavenumber displacement* from the monochromatic exciting radiation in the Raman spectrum.

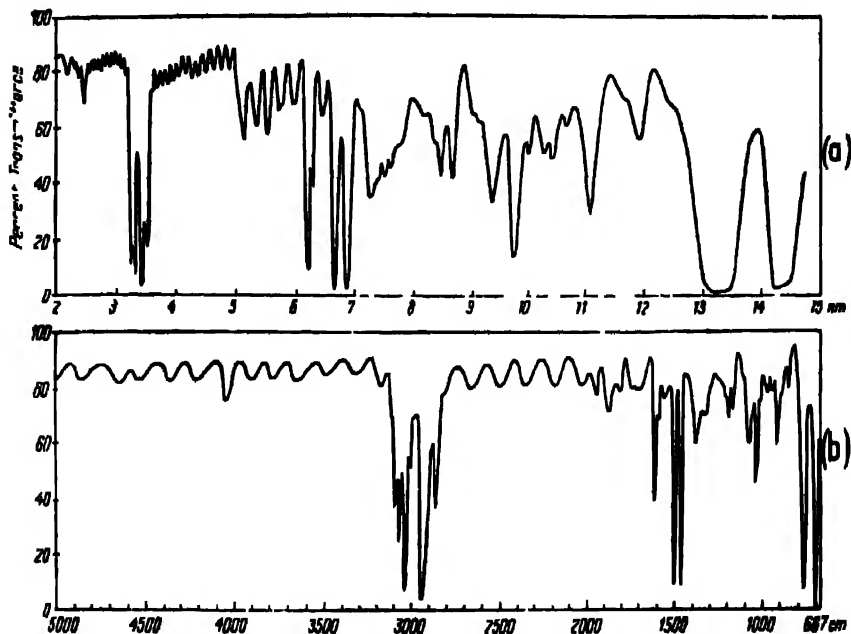


Fig. 1-51 Infrared spectrum of a polystyrene film: (a) linear wavelength scale; (b) linear wavenumber scale.

Thus, infrared and Raman spectra can be compared directly using a wave-number scale. No direct comparison is possible on a wavelength scale since the Raman band position changes grossly with the wavelength of the exciting radiation.

A priori it would seem rational that infrared spectra plotted on a wavenumber scale should also be represented with the scale increasing to the right. This, however, leads to a curve which is a reversal of the wavelength representation. By the time the wavenumber scale came into general use, there were already very extensive collections of infrared spectra in atlases and it was highly desirable that the overall appearance of the wavelength and wavenumber based infrared spectral charts be maintained as closely as possible. There were also instrumental design factors of an engineering nature that predisposed to the retention of the same direction of scan, and it is a combination of these factors that has led to the widespread adoption of a standard spectral format in which the wavenumber scale decreases from left to right.

Concerning the ordinate scale, a great many spectra are plotted as per cent transmission increasing upwards. If this is done, care must be taken when using the terms „minima“ and „maxima“. The chemical spectroscopist is interested mainly in the positions and intensities of the absorption maxima and incongruity arises since these appear on the charts as „transmission minima“, though this term is rarely, if ever, used in discussion. An appreciable minority avoid this by the simple expediency of plotting the per cent transmission on a scale from 100 to 0 increasing upwards and often this is accompanied by a change of name to per cent absorption; a tacit assumption is made here that all radiation not transmitted has been absorbed by the sample. Absorbance or molar absorption coefficient may also be plotted to yield curves with absorption peaks upwards but this also assumes that all radiation not transmitted by the sample has been absorbed. The fact remains that the quantity truly measured is the per cent transmission, but, except for the most precise quantitative work, objection to absorption-based scales is largely sophistry.

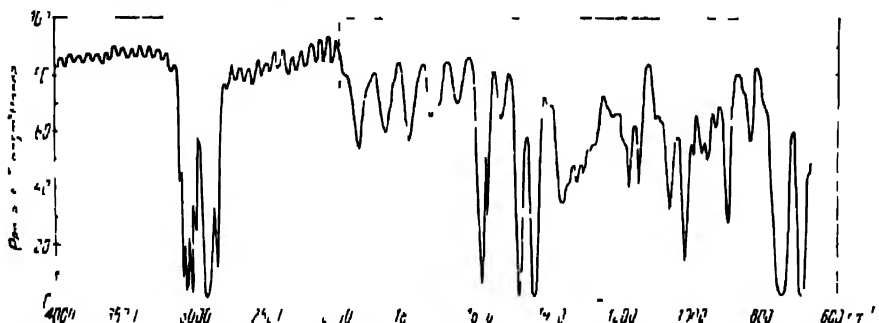


Fig. 1-52 Infrared spectrum of polystyrene with reduced abscissa in the 2000–4000 cm^{-1} region

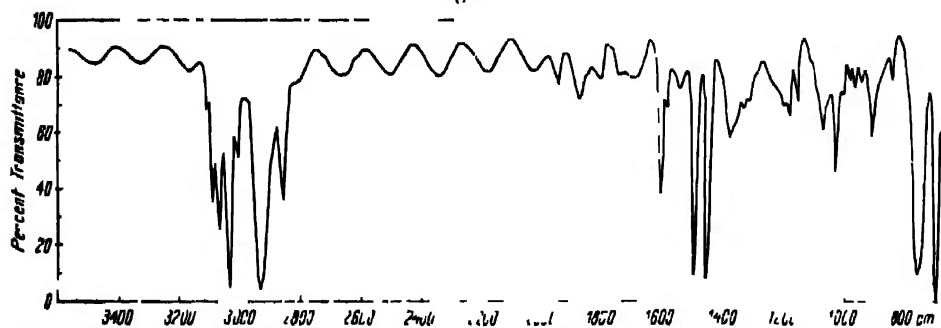


Fig. 1-53 Infrared spectrum of polystyrene recorded with a NaCl prism (667–2000 cm^{-1}) and a LiF prism (2000–3600 cm^{-1}).

8. The Shape and Intensity of Infrared Absorption Bands

An accurate description of an absorption band is given by plotting the molar absorption coefficient against the wavenumber (Fig. 1-51a). The band width is characterized by the number of reciprocal centimeters covered by

the band at an intensity level of $1/2 \epsilon_{\max}$. The quantity $\Delta\nu_{1/2}$ is called the *true half band width*. Since slits have a finite width, the observed band shape differs from the true one. The *apparent half band width* $\Delta\nu_{1/2}^{(a)}$ increases while $\epsilon_{\nu_{\max}}^{(a)}$ decreases with increasing slit width (Fig. I-54b). The maximum absorption coefficient $\epsilon_{\nu_{\max}}$ is a useful quantity for the characterization of band intensity. The $\epsilon_{\nu_{\max}}$ values of infrared absorption bands of organic compounds range from 1 to 1500.

Theoretically, the *integrated intensity* A of absorption bands is very important. This is the area covered by the absorption band. If one assumes that Beer's law is holding, the *absolute integrated band intensity* is given by

$$A = \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} b d\tilde{\nu} = \frac{1}{c l} \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \left(\frac{I_0}{I} \right)_{\tilde{\nu}} d\tilde{\nu}. \quad (\text{I-124})$$

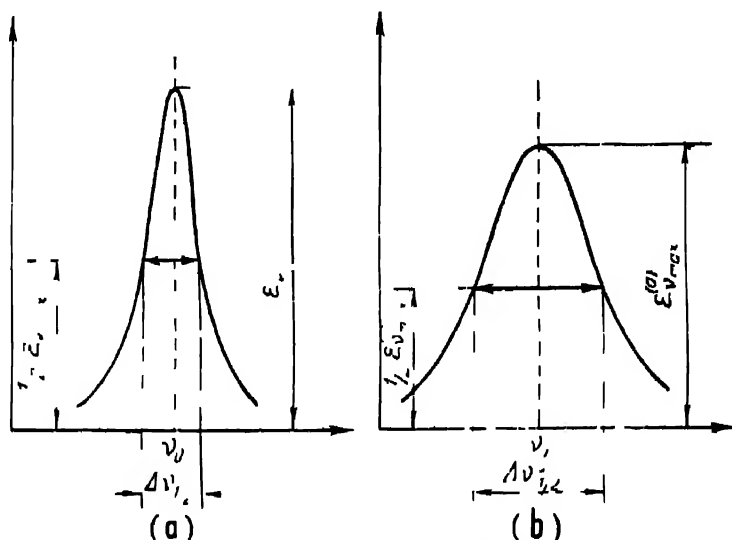


Fig. I-54 Shape and intensity of an infrared absorption band:
(a) true shape; (b) apparent shape, determined by the finite slit width.

Equation (I-124) originally proposed by Ramsay and Jones has been subsequently presented in modified form by several authors*. The units recommended provisionally by the Commission on Molecular Structure and Spectroscopy of IUPAC are:

a) An *absolute unit*, defined as

$$\frac{1}{c l} \int_{\text{band}} \ln \left(\frac{I_0}{I} \right)_{\nu} d\nu$$

* See footnote, p. 114.

where: c = concentration (molecule cm^{-3}),
 l = sample thickness (cm),
 ν = frequency (sec^{-1}).

This unit has the dimensions $\text{cm}^2 \text{ sec}^{-1} \text{ molecule}^{-1}$.

b) A *secondary unit*, defined as

$$\frac{1}{cl} \int_{\text{band}} \ln \left(\frac{I_0}{I} \right)_{\nu} d(\ln \nu).$$

This unit has the dimensions $\text{cm}^2 \text{ molecule}^{-1}$.

c) A *practical unit*, defined as

$$\int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \epsilon_{\tilde{\nu}} d\tilde{\nu}$$

where

$$\epsilon_{\tilde{\nu}} = \frac{1}{cl} \log_{10} \left(\frac{I_0}{I} \right)_{\tilde{\nu}}.$$

This unit has the dimensions $10^3 \text{ cm} \cdot \text{mole}^{-1}$.

Since the conditions of Beer's law cannot be perfectly achieved in practice, only the *apparent integrated intensity* B of a band can be obtained:

$$B = \frac{1}{cl} \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} \ln \left(\frac{I_0}{I} \right)_{\tilde{\nu}} d\tilde{\nu}, \quad (1-125)$$

where T_0 and T are the measured *apparent* radiant intensities before and after absorption by the substance at wavenumber ν . In this case the *apparent molar absorption coefficient* $\epsilon^{(a)}$ is

$$\epsilon^{(a)} = \frac{1}{cl} \log_{10} \left(\frac{T_0}{T} \right)_{\tilde{\nu}}, \quad (1-126)$$

and the apparent half band width is $\Delta\tilde{\nu}_{1/2}^{(a)}$.

For accurate determinations of band intensity, errors in concentration and path length must be as small as possible. The recording system must be linear. In order to avoid errors resulting from electrical and mechanical inertia of the detection and recording system, it would be ideal to measure the absorbance point by point, but this method would be too tedious. Generally, automatic recording at the lowest possible speed and with narrowest possible slits is used. In a detailed review of the subject, Seshadri and Jones* described and discussed the factors determining the true band shape, the determination of the true band shape from the apparent band shape, the evaluation of band intensity parameters, and the units for the measurements of integrated band intensities. Practical considerations in the choice of the optimum operating conditions have been discussed by Potts and Smith.**

* K. S. Seshadri and R. Norman Jones, *Spectrochim. Acta*, **19**, 1013 (1963), and literature cited therein.

** W. J. Potts, Jr., and A. Lee Smith, *Applied Optics*, **6**, 257 (1967).

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INFRARED SPECTRA OF THE PRINCIPAL CLASSES OF ORGANIC COMPOUNDS

As shown in the theoretical part, the infrared spectrum of a substance is determined by the nature, number, and relative positions of its atoms, i. e., by the structure of the molecule. Any change of a structural element implies a corresponding change in the spectrum. Thus the infrared spectrum appears to be one of the main physical characteristics of a substance. Because of their specificity, infrared spectra have been compared to fingerprints.

The first practical consequence of this property is the use of infrared spectra in the identification of substances by comparison with model spectra. A rich collection of such spectra is thus needed. The main collections and catalog of spectra published in recent years are mentioned on page 510. The spectra are printed on perforated cards which can be selected in minutes or even seconds by means of mechanical or electrical devices. The selection program is based on key data such as chemical functions, position, or intensity of bands, ring size, nature, and position of a substituent, etc.

Often the identification of intermediates and final products by means of infrared spectra may be an important auxiliary in reaction mechanism studies.

Any chemical impurity in a substance (except for those impurities that do not have infrared absorptions) leads to supplementary bands in the spectrum. A second analytical application of infrared spectroscopy is thus obvious, namely, purity control. The sensitivity of this method can be greatly improved by using the compensation procedure in double beam equipment as in the case of solvent compensation. The impure substance is introduced into the sample cell and an equivalent amount of solvent and pure substance are introduced into the reference cell. Thus one obtains the spectrum of the impurity. The procedure is called *differential spectroscopy*. By choosing the best recording parameters (maximum emission of the source, greater opening, adequate electronic amplification, extension of the ordinate), by careful work-up of the sample, and by utilization of an isolated and strong analytical band, traces of impurities (0.1–1%) can be determined with a precision as high as $\pm 0.01\%$.

A third very important application of infrared spectroscopy based on Beer's rule and the additivity of the molar extinction coefficients is quantitative analysis.

Most modern infrared spectrometers are equipped with devices that record the variation of transmission, absorption, or extinction as a function of

time at a given wavelength. Such recordings are used in kinetic studies of some chemical reactions.

Infrared spectra can be very helpful in solving problems dealing with molecular structure. The great majority of organic compounds consist of complex molecules. The frequency of their normal vibrational and rotational modes cannot be calculated. Because of this, spectrum-structure correlations are established almost exclusively in an empirical way by observing the existence and behavior of characteristic group frequencies. Extrapolation of results calculated for simple molecules may serve sometimes for the semi-quantitative interpretation of the structure of complex molecules. It is extremely important to know the reason for frequency shifts in various molecules. By studying infrared spectra of numerous homologs of a given series or of various substances belonging to different classes, it is possible to recognize the factors responsible for shifts of characteristic bands. In many instances it is possible to establish to what extent the spectrum of a given substance is influenced by electronic, mass, or steric effects as a function of molecular symmetry. Thus some hypothetical molecular models can be discarded, while others may be considered more or less probable.

The high precision of extinction measurements provided by modern instruments enables one to correlate the intensity of characteristic bands with molecular structure. It has been shown that in various structures, functions, or chemical bonds with not too different frequencies may generate bands with characteristic intensities.

It has to be pointed out that a molecular structure cannot be established solely on the basis of its infrared spectrum. The more complex the molecule, the more data are necessary. Sometimes elemental analysis, melting point or boiling point, the chemical reactions of a substance, its n. m. r., and mass spectra are all necessary in order to establish its structure.

Each of the applications mentioned above require a deep knowledge of the infrared spectra of various classes of organic compounds. In the following chapters the infrared spectra of the main classes of organic compounds are described in connection with the electronic structure and the steric configuration of the respective molecules.

CHAPTER 1

HYDROCARBONS

Absorption bands in infrared spectra of hydrocarbons arise from stretching and deformation vibrations of the carbon and hydrogen atoms forming the two types of grouping present: C—H and C—C.

The relatively constant position and the high intensity of CH linkages enable the identification and characterization of various types of CH bonds

and in many instances these absorptions are especially useful for analytical purposes.

C—C vibrations are theoretically very interesting but the usually low intensity, the coupling of vibrations, and the crowding of absorption bands in the respective region severely limit the characterization of such linkages.

The force constant of C=C and C≡C linkages is twice and three times, respectively as large as that of the C—C bond. Consequently, the respective bands

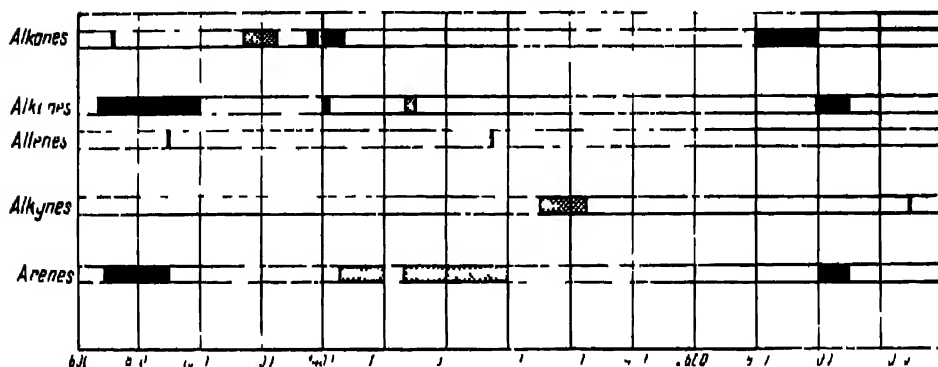


Fig. II-1 C—C frequencies (light) and C—H frequencies (dark) in hydrocarbons

arise at higher frequencies in less crowded regions and thus can be more readily identified.

The spectral regions containing the characteristic CH and C—C bands of hydrocarbons are shown in Fig. II-1.

The reduced mass of C—H groups is much smaller than that of C—C groups. Consequently, the bands arising from the stretching vibrations of the former occur at much higher frequencies (see Hooke's law, page 99).

The value of the force constant is highly dependent on the hybridization of the respective carbon atom. Thus it will determine a distinct differentiation of band positions in the region of CH stretching vibrations. As shown in Fig. II-1, enrichment in *s*-component from 1/4 to 1/3 and 1/2 in the series of linkages C—H, =C—H and ≡C—H, respectively, where hybridization changes from sp^3 to sp^2 to sp , results in higher frequencies because of the increased values of the force constant (the reduced mass remaining the same).

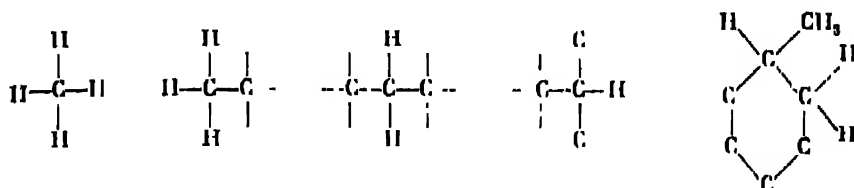
The bands arising from deformation modes occur in the region 600—1500 cm^{-1} . A differentiation between spectral zones corresponding to saturated and unsaturated CH linkages is also possible here.

A SATURATED HYDROCARBONS

1. General aspects

In saturated hydrocarbons, the carbon atoms linked by simple covalent bonds can form linear, branched, or cyclic chains. The hydrogen atoms form C—H linkages in methyl, methylene, or methine groups when attached to

primary, secondary, or tertiary carbon atoms, respectively. Methane displays a special character since it consists of a single carbon atom with its four tetrahedrally oriented valencies saturated by four hydrogen atoms.



Vibrational frequencies of C—H bonds are very different from those of C—C bonds mainly, because of the large mass differences of the atoms forming the respective bonds (see page 102).

In infrared spectra, vibrations arising from C—H linkages of methyl and methylene groups do not occur individually. The atoms of these groups oscillate simultaneously forming a compact vibrational group which generates unique absorptions for every type of vibration. The frequencies and intensities of these vibrations have been extensively investigated and are of value for the identification of the respective groups as well as for quantitative determinations.

Skeletal C—C linkages are less characteristic in the infrared. Vibrations of these bonds generate weak absorptions at lower frequencies. Accurate assignment of bands is difficult even for the simplest members. Identification of skeletal vibrations in higher members is practically impossible at present. Complications arise mainly because of numerous possibilities of coupling of vibrations with practically identical frequencies, arising from C—C linkages from various parts of the molecule as well as by the coupling of C—C linkages with some C—H linkages. Conformational isomerism is another factor preventing complete theoretical interpretation of spectra of saturated acyclic hydrocarbons or of large ring hydrocarbons.

The great majority of straight chain alkanes and isoalkanes in solution, liquid phase, or gas phase are not individual molecular species. They consist of a mixture of two or more *conformational isomers (conformers, rotamers)* arising from restricted rotation about simple C—C bonds. The possibilities of isomerism increase with chain length. Every conformer having a different symmetry will generate its groups of bands which are more or less characteristic. Because of vibrational coupling and superimposition of bands, the spectra of higher members contain a background frequency in this region which cannot be resolved by present means. The characteristic frequencies of C—H groups are practically the same for all conformers; differences arise in skeletal vibrations (C—C). The activity of these vibrations in the infrared is determined by molecular symmetry. The study of individual isomers is confined for the moment to simple molecules or to the solid phase, in which normal alkanes have a single *trans* zigzag conformation as shown by X-ray studies. In some instances, studies of conformational isomers in cycloalkanes with various ring sizes

were more successful. Compared to acyclic analogs with the same number of carbon atoms, cyclic compounds have fewer possibilities of conformational isomerism due to either the rigidity of molecules in small rings or to the preferential thermodynamic stability of certain conformers in larger rings.

The interpretation of spectra of saturated hydrocarbons is based on theoretical studies of simple homologs as well as on comparative studies of a great number of hydrocarbons with various structures. In spite of the complications mentioned above, many problems in alkane chemistry can be solved by using data obtained from infrared spectra.

After describing the principal types of C—H vibrations in hydrocarbons, we discuss the general aspects, position, and intensity of absorption bands in normal alkanes, isoalkanes and cycloalkanes with condensed rings.

a. **Vibrations of C—H linkages.** The vibrational modes of the three types of C—H linkages in saturated hydrocarbons are described separately. Methine, methylene, and methyl groups are considered as independent systems with respect to their vibrations [1,2].

1. **Vibrations of the tertiary CH group.** The methine group has a single *stretching vibration* (Fig. II-2a) and two *deformation vibrations*: in-plane and out-of-plane (Fig. II-2b and c) (generally doubly degenerate).

>C—H bonds arise only in isoalkanes, substituted cycloalkanes, or in polycyclic compounds.

2. **Vibrations of the CH_2 group.** This group gives rise to two *stretching vibrations* and four *deformation vibrations* (Fig. II-3). The two stretching modes can be symmetrical (νCH_2 sym) or asymmetrical (νCH_2 asym), corresponding to the in-phase or out-of-phase vibrations, respectively of the hydrogen atoms (Fig. II-3 a,b).

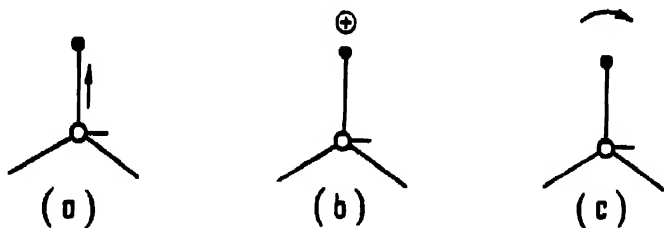


Fig. II-2 Vibration modes of the methine group.

The deformation vibration can take place in-plane or out-of-plane of the CH_2 group.

The in-plane vibrations which alter the $\text{H—}\hat{\text{C}}\text{—H}$ angle are known as *scissoring vibrations* (δCH_2) (Fig. II-3c). Those that do not alter this angle are known as *rocking vibrations* (γCH_2) (Fig. II-3d).

The *out-of-plane* deformation modes can take place either as a *wagging* in which both atoms move in phase above or below the plane of the CH_2 ,

*group ($\delta\text{CH}_2/w$) (Fig. II-3e), or as a twisting ($\delta\text{CH}_2/t$) (Fig. II-3f), in which one atom moves above the plane and the other atom moves below the plane.

3. *Vibrations of the CH_3 group.* In the symmetrical stretching mode, νCH_3 sym, the three C—H linkages are lengthened and contracted in phase (Fig. II-4a). The asymmetrical stretching mode νCH_3 asym takes place by lengthening of two of the C—H bonds and simultaneous shortening of the third bond (Fig. II-4b).

In the nonplanar methyl group two deformation modes are possible (δCH_3): a symmetrical deformation mode (δCH_3 sym) (symmetrical bending), when all

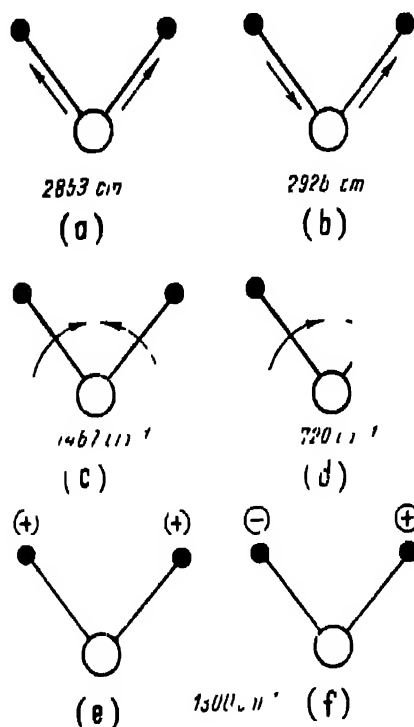


Fig II-3 Vibration modes of the methylene group

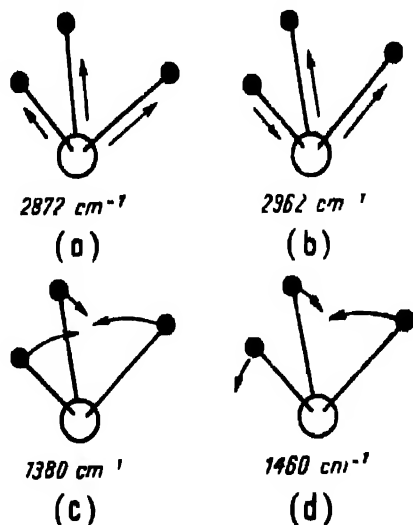


Fig II-4 Vibration modes of the methyl group

hydrogen atoms are drawn further or closer apart from the axis in phase (Fig. II-4c) and an asymmetrical deformation mode (δCH_3 asym), when two of the hydrogen atoms move inwards and the third one outwards and vice versa (Fig. II-4d). Another vibrational mode of the methyl group is the so-called *methyl rocking* resulting from the association of the two deformation modes with the vibration of the C—CH₃ linkage. One should also mention the twisting of the entire CH₃-group about the C—CH₃ linkage.

b. *Vibration of C—C linkages.* Stretching and deformation vibrations of C—C linkages forming the skeleton of straight chain polymethylenic hydrocarbons may be visualized as movements of an accordion. These vibrations are highly coupled and give rise to weak absorptions. Although very interesting

in studies of molecular structures, the vibrational analysis of C—C linkages is practically impossible. Some attempts to assign bands in alkanes and isoalkanes have been made [1,3]. Better results were obtained with Raman spectra.

2. Saturated acyclic hydrocarbons

a. Straight-chain alkanes

The knowledge of alkane spectra is very important for organic chemistry. The characteristic units of these hydrocarbons are found in the vast majority of organic molecules.

In the case of the first members of the C_nH_{2n+2} series, accurate assignments of bands could be made by complete vibrational analysis [4].

a. **Methane and ethane.** *Methane* is the only hydrocarbon in which the four valencies of the carbon atom with ideal sp^3 hybridization are oriented according to van't Hoff's tetrahedral model. Vibrational analysis of the methane and deuteriomethane molecule, as well as the study of infrared and Raman spectra, are in agreement with this model [4].

If treated as a system of five tetrahedrally oriented points, methane can be assigned to the cubic group T_d (see Fig. I-29). Of the nine possible vibrational modes, two are doubly degenerate (E) and six are triply degenerate (F_2). This results in four fundamental vibrations shown in Table II-1.

Table II-1 Fundamental vibrations in CH_4 and CD_4 [2]

| Assignment and species of vibrations | Frequency cm^{-1} | | Activity | Kind of vibration |
|--------------------------------------|---------------------|--------|----------|-------------------|
| | CD_4 | CH_4 | | |
| $\nu_1(A_1)$ | 2084.7 | 2914.2 | R | νCH sym |
| $\nu_2(E)$ | 1054 | 1526 | R | δHCH asym |
| $\nu_3(F_2)$ | 2258.2 | 3020.3 | IR R | νCH sym |
| $\nu_4(F_2)$ | 995.6 | 1306.2 | IR | δHCH asym |

Of these modes ν_1 and ν_2 are active only in Raman spectra. ν_3 is active both in Raman and the infrared; ν_4 is active only in the infrared (Fig. II-5).

The activity of these vibrations is in agreement with the tetrahedral model predicted for the methane molecule. Any other configuration, for example, planar (with D_{4h} symmetry) or pyramidal (C_{4v}), both of which can be excluded because of lack of isomerism in disubstituted compounds [5], should give rise to a larger number of infrared active bands. The tetrahedral model is also in agreement with the rotational structure of the bands [6].

In *ethane* [7,8] a skeletal C—C vibration is also possible. However, because of molecular symmetry, this vibration is active only in the Raman spectrum (at 993 cm^{-1}). The structure of ethane has been thoroughly discussed. The analysis of vibrational spectra of ethane C_2H_6 and deuterioethane C_2D_6 does not show the existence of free rotation about the C—C bond. Of the two possible conformers (see below), one with eclipsed conformation D_{3h} (12 fundamental vibrations, 9 active in Raman) and the other with stag-

gered conformation with a center of symmetry, D_{3d} (12 fundamental vibrations, 6 active in Raman), the molecule adopts the latter, which is energetically more favored. Thus only one of the two possible conformers is actually observed. The eclipsed isomer appears as a transient form in extremely low concentration.

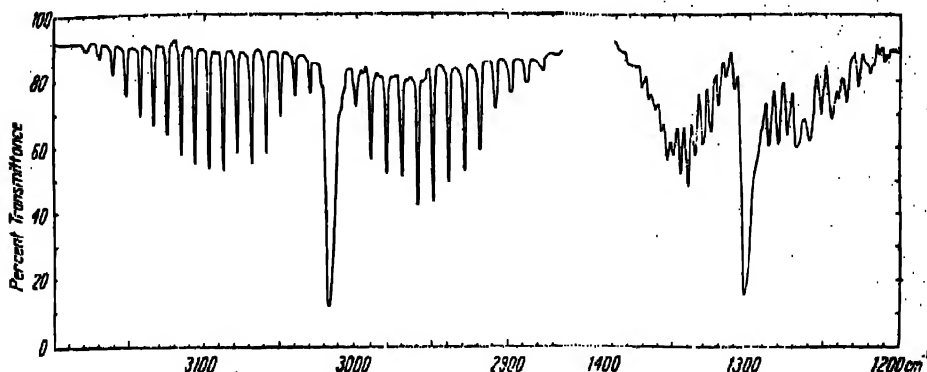


Fig. 11-5 Infrared spectrum of methane (gas).

The stretching and deformation vibrations of C—H linkages in the two methyl groups are those characteristic of C—H linkages in alkanes.

For higher members of the C_nH_{2n+2} series, accurate theoretical treatment becomes very complicated. Each of the saturated acyclic hydrocarbons has $9n$ vibration modes corresponding to stretching vibrations of C—H and C—C bonds and to deformation vibrations $H-\hat{C}-H$, $H-\hat{C}-C$, and $C-\hat{C}-C$. The spectral regions containing bands arising from these vibration are shown in Table II-2 [9].

The number of fundamental vibrations actually active in infrared and Raman spectra is determined by the symmetry of the corresponding conformational isomers.

Table II-2 The number of normal vibration modes in C_nH_{2n+2} hydrocarbons

| Symbol | Type of vibration | No. of normal vibration modes | Region, cm^{-1} |
|----------------------|--|-------------------------------|-------------------|
| $\nu C-H$ | Stretching vibrations C—H | $2n+2$ | 2800 — 3000 |
| $\nu C-C$ | Stretching vibrations C—C | $n-1$ | 800 — 1200 |
| $\delta H-\hat{C}-H$ | Deformation vibrations $H-\hat{C}-H$ (6 modes of the two CH_3 groups and $n-2$ modes of the CH_2 groups) | $n+4$ | 1340 — 1460 |
| $\delta H-\hat{C}-C$ | Deformation vibrations $H-\hat{C}-C$ (4 modes of the two CH_3 groups and $3n-6$ of the CH_2 groups) | $3n-2$ | 520 — 650 |
| $\delta C-\hat{C}-C$ | Deformation vibrations $C-\hat{C}-C$ | $n-2$ | 150 — 520 |
| $\delta C-Ct$ | Twisting vibrations about the $n-1$ C—C bonds | $n-1$ | 200 — 300 |

b. **Conformational isomers.** Spectral interpretation of many alkanes is complicated by the fact that in solution, in liquid, or in gaseous phase these substances exist as a mixture of two or more *conformational isomers* (rotamers).

Free rotation about the simple C—C bond is extremely rare. Because of repulsion between hydrogen atoms when passing in front of each other, most of the time the molecule adopts forms with the lowest potential energy. These forms are *rotational* or *conformational isomers* [10]. In solution, less energy is required for the interconversion of rotamers; therefore they coexist in ratios dependent on temperature, dilution, etc. Rotational isomers cannot be isolated chemically although they are distinct molecular species. However, they can be detected by investigation of changes in vibrational spectra with temperature.

In the simple case of ethane, consisting of two symmetrical methyl groups, the molecule can adopt two conformations: *eclipsed* (Fig. II-6e) and *staggered* (Fig. II-6s).

The variation of potential energy in a 360° -rotation is shown in Fig. II-7. The staggered forms are lower in energy than the eclipsed forms. Consequently, the molecule will adopt the more stable staggered forms. In ethane, because of the equivalence of the two moieties, the three perfectly equivalent staggered conformations cannot be distinguished spectroscopically. These conformations can be distinguished if one modifies the trigonal symmetry of the methyl

Fig. II-6 Conformations of ethane represented in three different ways: (e) eclipsed conformation; (s) staggered conformation.

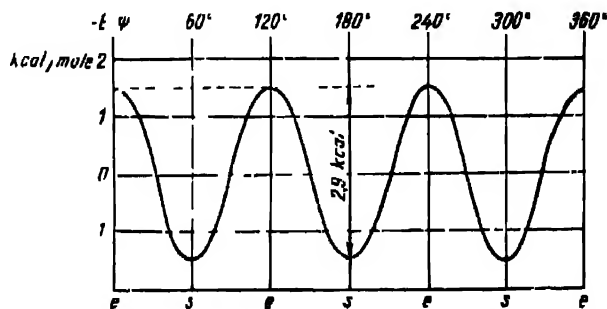


Fig. II-7 Potential energy variation as a function of the angle of rotation ϕ in the ethane molecule: (e) eclipsed conformation; (s) staggered conformation.

groups by substitution. In compounds $X-CH_2-CH_2-X$, the three staggered conformations differ from each other with respect to the reciprocal positions of the two $C-X$ linkages.

The existence of conformational isomers was established by studies of Raman [11] and infrared spectra [12, 13]. It was first observed in the case

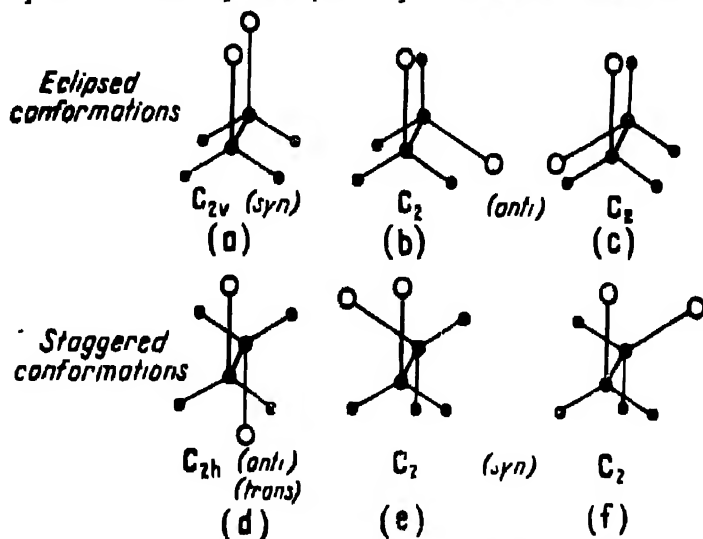


Fig. 11-8 Conformations of *n*-butane (C_{2v} , C_2 , C_{2h} point groups).

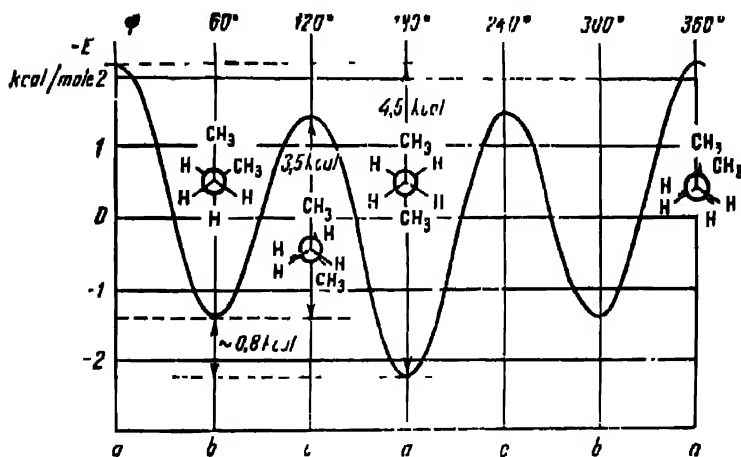


Fig. 11-9 Variation of potential energy with angle ϕ in the butane molecule:

(a) *syn*-eclipsed conformation; (b) *syn*-staggered; (c) *anti*-eclipsed conformation; (d) *anti*-staggered.

of butane. The mathematical treatment of the *n*-butane molecule can be simplified if one considers the molecule as a disubstituted ethane [14, 16]. The theoretically possible conformations are shown in Fig. 11-8 and 11-9.

Corresponding to eclipsed conformations (Fig. 11-8 *a-c*) are a *syn* form with C_2 symmetry and two equivalent *anti* forms with C_2 symmetry [18*a*]. In another nomenclature, the eclipsed *syn* conformation is called *cis* and the eclipsed *anti* conformation is called *gauche* [18*c*]. The variation of potential energy with rotation about the C_2-C_3 bond is shown in Fig. 11-9. The staggered conformations have the lowest potential energy. Consequently, the molecule will adopt one of the three staggered conformations (Fig. 11-8*d-f*).

The staggered *anti* conformation (Fig. 11-8*d*) has a single *trans* form with two opposite CH_3 groups resulting from rotation of the CH_3-CH_2 units (considered rigid) by 180° with respect to each other. However, two equivalent *syn* forms are possible (Fig. 11-8*e, f*), resulting from rotation of one of the two moieties by 120° or 240° , respectively [17, 18].

The *anti* conformation with a center of symmetry C_{2h} -- precludes simultaneous activity of vibrations both in the infrared and Raman. Experimentally, it has been shown that the infrared and Raman spectra of butane in the solid state at low temperature consist of very few bands. This corresponds to a more symmetrical *anti* conformation with lower energy and greater stability. On raising the temperature [13, 19] the *syn* forms, higher in energy, occur in equilibrium with the *anti* forms. The presence of additional molecular forms with less symmetrical (*syn*) conformations in the spectra of liquid and gaseous butane results in an increased number of bands.

X-ray studies [20] have shown that the higher members of the C_nH_{2n+2} series in the crystalline state have a planar *trans*-zigzag conformation corresponding to the staggered *anti* conformation. In the liquid state or in solution, several isomers are present; consequently the spectra of liquids and solutions are more complicated. In the most favorable case the liquid contains only one more stable form than the solid. By measuring the variation of band intensities of the two forms at various temperatures, it is possible to determine the differences in their energy with the same precision as from thermodynamic data [12, 13].

In even-numbered straight chain alkanes with a center of symmetry, the rule of mutual exclusion precludes coincidences between some infrared and Raman bands. In odd-numbered chains, coincidences are allowed. In long chain polymethylenes, symmetries cannot be determined by methods applied in simple molecules. New adaptations of these classical methods are now being developed for these systems [2, 21].

Current recordings of spectra are done in the liquid state or in solution, i. e., with mixtures of conformational isomers. Although in theory each isomer has its own characteristic group of bands, the exact assignment of frequencies is not possible. This is primarily because of the similarity of spectra of hydrocarbons with more than five carbon atoms. The very important skeletal (C-C) vibrations are not well defined even in small molecules. Vibrational coupling in longer chains precludes the assignment of individual frequencies in most cases. Thus only characteristic bands arising from stretching and deformation

vibrations of C—H linkages are of practical value in studies of the infrared spectra of normal alkanes.

c. **Absorption bands in higher alkanes.** The investigation of a large number of acyclic saturated hydrocarbons enabled the accurate assignment of absorption bands arising from CH_3 , CH_2 , and CH groups [1, 22–24].

There are two categories of C—H vibrations. The first encompasses vibrations with frequencies which are constant for the great majority of studied compounds; these vibrations are only slightly influenced by the rest of the molecule. Stretching vibrations and some deformation vibrations, for example, the scissoring vibration of the CH_2 group and the symmetrical and asymmetrical deformations of the methyl group, belong to this category. The other deformation modes are influenced by the rest of the molecule and mainly because of coupling have variable frequencies. Their identification is more difficult and less reliable.

d. **C—H stretching vibrations.** C—H stretching vibrations give rise to strong absorptions in the $2800\text{--}3000\text{ cm}^{-1}$ region. A monochromator with satisfactory resolution is able to detect at least four absorption bands arising from C—H stretching vibrations of acyclic saturated hydrocarbons. These bands are assigned to CH_3 and CH_2 groups.

1. **CH_3 Group.** The frequency of the *symmetrical stretching vibration* νCH_3 , sym is 2872 cm^{-1} and that of the *asymmetric stretching vibration* νCH_3 , asym is 2962 cm^{-1} . In straight chain saturated hydrocarbons the variation from these values was not more than $\pm 10\text{ cm}^{-1}$ (Table II-3).

Table II-3 νCH_2 and νCH_3 bands in straight chain saturated hydrocarbons [25]

| Hydrocarbon | State | νCH_2 , cm^{-1} | | νCH_3 , cm^{-1} | |
|------------------------------|-----------------------------|-------------------------------------|------|-------------------------------------|-------|
| | | asym | sym | asym | sym |
| $\text{C}_{12}\text{H}_{26}$ | liquid | 2924 | 2852 | 2957 | 2873 |
| | solid | 2918 | 2847 | 2953/8 | 2871 |
| $\text{C}_{16}\text{H}_{34}$ | liquid | 2925 | 2854 | 2937 | 2873 |
| | solid | 2916 | 2849 | 2955 | |
| $\text{C}_{22}\text{H}_{46}$ | solution (CCl_4) | 2927 | 2854 | 2955 | 2872 |
| | solid | 2916 | 2849 | 2954/60 | 2872 |
| $\text{C}_{28}\text{H}_{58}$ | solid | 2918 | 2850 | 2955 | |
| $\text{C}_{32}\text{H}_{66}$ | solution (CCl_4) | 2927 | 2953 | 2954- | 2860- |
| | | | 2855 | 2958 | 2872 |

A careful study of straight chain alkanes [24] shows that the stretching vibration of the terminal CH_3 group is not greatly altered in position in going from the liquid state or solution to the solid state.

It was found that in some *n*-alkanes in the crystalline state, the band arising from the asymmetrical stretching mode of the CH_3 group is split into a doublet [25]. *n*- $\text{C}_{12}\text{H}_{26}$ and *n*- $\text{C}_{22}\text{H}_{46}$ have a νCH_3 , asym doublet at 2953 and 2958 cm^{-1} . In the spectrum of *n*- $\text{C}_{22}\text{H}_{46}$, the doublet was previously reported at 2958–2965 cm^{-1} [25]. In these hydrocarbons the doublet

seems to be a consequence of the triclinic crystalline modification since Δ appears also in the triclinic modifications of heptadecanoic acid [26].

For the C_nH_{2n+2} series with $n=6, 7, \dots, 36$ the values for νCH_3 asym are $2954-2958\text{ cm}^{-1}$ and for CH_3 sym $2869-2872\text{ cm}^{-1}$.

2. CH_2 Group. The symmetrical stretching vibration, νCH_2 sym of the methylene group gives rise to an absorption band at ca 2853 cm^{-1} . The band of the asymmetric vibration arises at ca 2926 cm^{-1} . As in the case of the methyl group, variation from these values is very small in saturated straight chain hydrocarbons. A comparative study of spectra of straight chain alkanes with 6–36 carbon atoms [24] shows that the frequency of the asymmetric stretching vibration of the CH_2 group is $\sim 10\text{ cm}^{-1}$ and that of the symmetric vibration $\sim 5\text{ cm}^{-1}$ higher in the liquid state or in solution than in the solid state (Table II-3).

3. Intensity of νCH bands. The relative intensity of νCH absorption bands depends on the ratio of CH_2 and CH_3 groups in the alkane molecule.

Qualitatively, it is observed that bands arising from asymmetrical stretching vibrations at 2926 cm^{-1} and 2962 cm^{-1} for CH_2 and CH_3 groups, respectively, are stronger than the symmetrical vibrations of these groups. By measuring the intensities of these bands it is possible to determine the

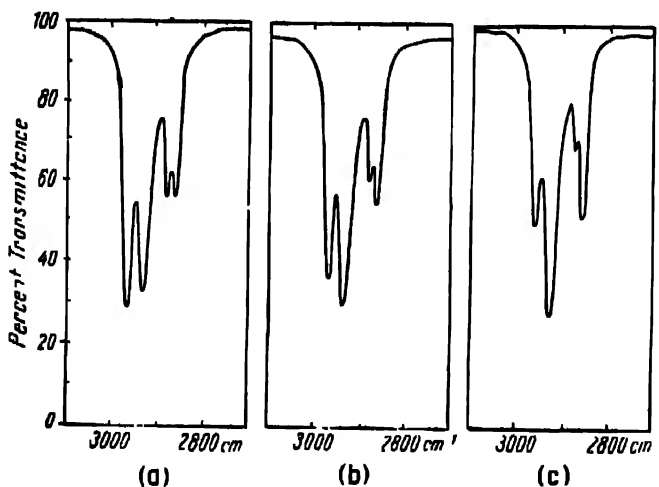


Fig. II-10 Infrared spectra of some straight chain alkanes in the C-H stretching mode region.

(a) *n*-hexane; (b) *n*-heptane; (c) *n*-decane.

number of CH_2 or CH_3 groups in the molecule; such measurements can be very helpful in molecular structure determinations.

In straight chain saturated hydrocarbons with more than four carbon atoms, the intensity of bands arising from CH_2 groups increases with chain lengths, i.e., with the number of CH_2 groups. The CH_3 group does not show a similar variation. In Fig. II-10 are shown infrared spectra of straight chain alkanes with an

increasing number of CH_2 groups. It can be seen that in longer chains (with an increased $\text{CH}_2:\text{CH}_3$ ratio) the relative intensity of νCH_2 bands decreases [27].

Molar extinction coefficient measurements [27] in *n*-alkanes with 6–36 carbon atoms showed an increment of 75 units per CH_2 group for the 2926 cm^{-1} band of 45 units per CH_2 group for the 2853 cm^{-1} band. The CH_3 group has smaller increments.

The intensity of the νCH_2 asym band at 2926 cm^{-1} increases steadily with the number of the CH_2 groups [24].

As a result of more accurate quantitative studies based on integrated absorption intensity measurements in many straight chain and branched alkanes [28], the following relation was proposed:

$$N = N_{\text{CH}_3}a + N_{\text{CH}_2}b + N_{\text{CH}}c$$

where N_{CH_3} , N_{CH_2} , N_{CH} are the number of C–H linkages in methyl, methylene and methine groups and a , b , and c are proportionality coefficients equal to 4.112, 3.809, and 1.388 respectively. This relation enables the determination of the number of CH_3 , CH_2 , and CH groups in the molecule. The calculated intensities for the integrated absorption are in agreement with experimental values for straight chain alkanes.

The above relation is not applicable to more complex branched hydrocarbons because of increased interactions between CH_3 , CH_2 and CH groups. For these cases results are obtained by measuring the intensities at 1375 cm^{-1} for the methyl group and at 890 cm^{-1} for the ethyl group.

Although, generally speaking, the additivity of band intensities arising from CH groups is maintained in any hydrocarbon chain, the values obtained for *n*-alkanes are not rigorously reproducible in other classes of organic compounds (see following chapters). The presence of polar atoms alters the force constant (frequency) and intensity of bands arising from vibrations of C–H linkages in adjacent groups.

Figure II-11 is a schematic representation of position and relative intensities of absorption bands arising from stretching vibrations of CH_3 , CH_2 , and CH groups in straight chain saturated hydrocarbons. The characteristic alternation of frequencies arising from methyl and methylene groups, as well as the higher intensity of asymmetric νCH stretching modes, can be observed.

c. **Deformation vibrations.** Assignments of bands corresponding to deformation modes of CH_3 and CH_2 groups are based not only on comparisons of a great number of spectra of hydrocarbons but also on data obtained from mathematical analysis of vibrations in simple hydrocarbons.

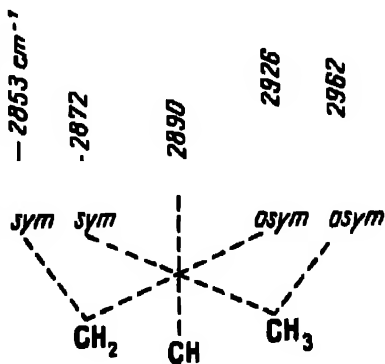


Fig. II-11 Partition of saturated CH bands in the $2800\text{--}3000 \text{ cm}^{-1}$ region. The line height shows approximately the mean relative intensities.

As shown above, there are a number of deformation vibrations with almost constant frequencies, for example, those taking place with changes in bond angles (scissoring vibrations of the CH_2 group and the two deformation vibrations of the CH_3 group). The other deformation modes are affected to a certain extent by adjacent structural elements. Changes in position and intensity of these bands are due to coupling with other C-H deformation vibrations or with skeletal carbon-carbon stretching vibrations. Thus it is difficult to assign exact limits to the characteristic regions for these vibration modes.

1. CH_3 group. The symmetrical deformation mode of the methyl group (Fig. II-4c) gives rise to an absorption at $1365 - 1380 \text{ cm}^{-1}$.

The exact assignment of the frequency corresponding to this vibration is based on studies of mass effects obtained by deuteration. In ethane [6, 7] the δCH_3 sym band arises at 1379 cm^{-1} . In C_2D_6 this band disappears, being replaced by an absorption corresponding to the δCD_3 sym mode at 1072 cm^{-1} .

In spectra of *n*-alkanes the position of the δCH_3 sym band is relatively constant. This band is of great analytical value, since this region does not contain other strong absorptions.

Investigation of straight chain alkanes from C_{20} to C_{30} [29] has shown that the frequency corresponding to the δCH_3 sym mode is independent of the crystalline state. It depends on whether there are an even or odd number of carbon atoms in the molecule. In even-numbered chains this frequency arises at $1365 - 1368 \text{ cm}^{-1}$, while in odd-numbered chains it has slightly greater values, ranging from $1373 - 1376 \text{ cm}^{-1}$ [25].

The occurrence of these bands in infrared spectra of long chain paraffins may indicate the existence of a branched structure. In polyethylene the band arising from the δCH_3 sym vibration occurs at 1375 cm^{-1} [30, 31]. This band can be used for estimating the number of methyl groups in the molecule [24]. Investigation of band intensities at 1375 cm^{-1} (δCH_3 sym) and 2958 cm^{-1} (νCH_3 asym) enabled the determination of the degree of branching in some commercial types of polyethylene by comparison with polyethylene prepared from diazomethane or by polymerization at atmospheric pressure [30].

The analysis of the δCH_3 sym band is important in studies of compounds containing structural elements capable of affecting the vibration of this group (O, S, C=C, etc.).

The asymmetric deformation vibration of the methyl group shown in Fig. II-1d gives rise to a band around 1460 cm^{-1} . The proximity of this frequency to that of the scissoring vibration of the methylene group prevents it from being used in reliable identifications of CH_3 groups in compounds of unknown structure.

In spectra of low molecular weight alkanes where $\text{CH}_3:\text{CH}_2$ ratios are high, the δCH_3 asym band can be distinguished from that assigned to the methyl group [32].

In spectra of medium chain alkanes it appears as a shoulder on the δCH_2 -band (Fig. II-12a-c). In long chain alkanes the distinction is no

longer possible because of the increased number of CH_2 groups versus CH_3 groups. The identification of the δCH_3 asym vibration in this region in the presence of the scissoring δCH_2 vibration is possible in cases when one of these bands is shifted away from its normal position (see strained cycloalkanes, ketones, acids, esters, etc.).

Other deformation vibrations of the CH_3 group. Absorptions arising from CH deformation modes strongly coupled with C—C skeletal vibrations are

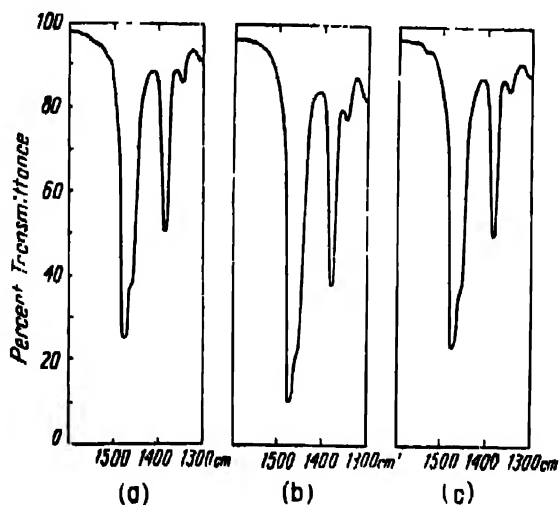


Fig. 11-12 Infrared spectra of some *n*-alkanes in the region of C-H deformation vibrations:
(a) *n*-hexane; (b) *n*-heptane; (c) *n*-decane.

not constant in position in different classes of alkanes. They arise in the region $800\text{--}1250\text{ cm}^{-1}$. Thus in ethane the frequency of the in-plane rocking vibration of the methyl group coupled to that of the C—C bond, $\text{CH}_3\text{—C}$ (methyl rocking), is 1190 cm^{-1} [32, 34] while in propane it is believed to be 1155 cm^{-1} [1]. In *n*-butane this vibration is theoretically forbidden on grounds of molecular symmetry [1, 19].

In spectra of straight chain alkanes with 4–18 carbon atoms recorded in the liquid state or in solution, this vibration is considered to give a weak band at $1132\text{--}1141\text{ cm}^{-1}$ [34]. The intensity of this band is too weak to be identified in spectra of straight chain hydrocarbons with more than 20 carbon atoms. In the crystalline state a difference between even- and odd-numbered alkanes was observed. A band of medium intensity arises only in spectra of odd-numbered alkanes [35]. In those with even numbers this vibration mode is inactive in the infrared.

The twisting mode $\text{CH}_3\text{—C}$ is due to restricted rotation of the methyl group coupled with the vibration of the C—C linkage. It arises at low frequencies, below 300 cm^{-1} , and has not been thoroughly investigated.

2. CH_2 group. The scissoring vibration (Fig. II-3c) is the most characteristic deformation mode of the CH_2 group. In spectra of *n*-alkanes it gives rise to a strong absorption at 1467 cm^{-1} . This band overlaps with that of the asymmetric deformation mode of the CH_3 group at 1460 cm^{-1} (see page 122). Its position is influenced by adjacent structural elements. The intensity increases with the number of CH_2 groups. As in the case of stretching vibrations, measurements of molar extinction coefficients or integrated absorption enable the determination of the CH_2/CH_3 ratio and thus the lengths of the hydrocarbon chain [28].

In-plane rocking vibration of the CH_2 group (γCH_2) (Fig. II-3d). Spectra of straight chain alkanes with more than five carbon atoms recorded in solution or in the liquid state show a medium intensity band at $720 \pm 2\text{ cm}^{-1}$ assigned to γCH_2 modes. In lower members the frequency increases moderately. This region is of value for the identification of polymethylenic chains. It has been shown that straight chain hydrocarbons with four carbon atoms give rise to a strong band at 740 cm^{-1} , while in those with three carbon atoms on an ethyl group, this band arises at 770 cm^{-1} . This enables the identification of neighboring two, three, four, or five CH_2 groups in side chains of complex steroidal molecules [36]. In the crystalline state a splitting of the γCH_2 band is observed in most cases. Instead of a single absorption at $720 \pm 2\text{ cm}^{-1}$, two bands of unequal intensities are observed at 721 and 730 cm^{-1} . This splitting was attributed by some authors to molecular interactions in the crystalline phase [37]. Investigation of the behavior in the infrared of a great number of alkanes (C_{11} – C_{64}) in the solid state showed the significance of the crystalline modification of the hydrocarbon in this phenomenon [25].

The rocking vibrational almodes of the CH_2 group in a series of crystalline *n*-alkanes are shown in Table II-4.

Table II-4 Rocking vibration of the CH_2 group [25, 29]

| Hydrocarbon (<i>n</i> -alkane) | Crystalline modification | γCH_2 , cm^{-1} | Other references | Hydrocarbon (<i>n</i> -alkane) | Crystalline modification | γCH_2 , cm^{-1} | Other references |
|------------------------------------|-----------------------------|---|---------------------|------------------------------------|-----------------------------|---|---------------------|
| C_{11} | Orthorhombic | 720 728 | [38] | C_{29} | Triclinic | 721 | |
| C_{13} | Orthorhombic | 723 734 | [38] | C_{29} | " | 721 | |
| C_{17} | " | 718 728 | [39] | C_{34} | " | 721 | |
| C_{19} | " | 720 740 | [38] | C_{38} | " | 721 | |
| C_{21} | " | 722 735 | | C_{39} | Monoclinic | 719 731 | |
| C_{23} | " | 722 734 | | C_{40} | " | 722 735 | |
| C_{25} | " | 722 735 | | C_{44} | " | 720 730 | |
| C_{27} | " | 722 735 | | C_{48} | " | 719 731 | |
| C_{29} | " | 722 731 | | C_{54} | " | 721 731 | |
| C_{19} | Triclinic | 717 | | $\text{C}_{n}\text{H}_{2n+2}$ | Liquid or solution | 721 | [38–40] |
| C_{16} | " | 720 731 | | | | | |

Straight chain crystalline alkanes with an even number of carbon atoms C_{12} – C_{26} and triclinic symmetry show a single γCH_2 band at 717 cm^{-1}

[24] or 721 cm^{-1} [29]. In *n*-alkanes with an odd number of carbon atoms C_{11} – C_{29} and orthorhombic symmetry the band is split apart by $10 \pm 1\text{ cm}^{-1}$. In the hydrocarbon C_{10} the splitting is 20 cm^{-1} . Splitting is also observed in higher members (C_{28} – C_{34}) with even numbers of carbon atoms and monoclinic symmetry.

This difference in behavior depending on the crystalline modification has to be taken into account in analytical interpretations of the 720 cm^{-1} band in cases for which spectra are not recorded in solution [24, 29]. The occurrence of a band at 720 cm^{-1} in complex molecules does not necessarily prove the existence of chains containing more than four neighboring methylene groups as was previously thought.

In solutions of long chain hydrocarbons the apparent molar extinction coefficient increases linearly with the number of CH_2 groups with an increment of three units per group [41]. The νCH_2 asym band at 2920 cm^{-1} shows a similar behavior [20]. The intensity ratio of these two bands is independent of the number of methylene groups and is the same for all straight chain alkanes in the liquid state or in solution. However, the two bands become considerably stronger in the solid state [25]. In urea adducts of straight chain saturated hydrocarbons, the intensities of γCH_2 bands at 720 cm^{-1} and of νCH_2 asym bands at 2920 cm^{-1} are lower than in spectra of the same hydrocarbons in the solid state. Spectra of these adducts are rather comparable to those of the corresponding hydrocarbons in the liquid state or in solution. This leads to the assumption that in these types of adducts the hydrocarbon is linked to urea by van der Waals type bonds in the same way as alkane chains are linked in solution [25].

In long chain polymethylenic polymers the γCH_2 doublet can be used to determine the degree of crystallinity of the material. In solid polyethylene the frequencies of the two parts of the doublet are 721 and 730 cm^{-1} [30]. On cooling to 4°K the 730 cm^{-1} band becomes stronger, while the 721 cm^{-1}

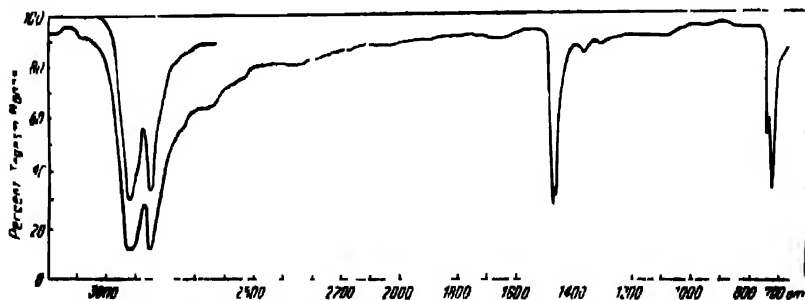


Fig. II-13 Infrared spectrum of polyethylene AS (degree of crystallinity $\sim 65\%$).

band remains the same. On melting, a large band centered at 721 cm^{-1} appears instead of the doublet.

The 730 cm^{-1} band was assigned to the crystalline portion of the macromolecule, while the 721 cm^{-1} band was assigned to the amorphous part

(containing, however, crystalline parts in the melt). Figure II-13 shows the spectrum of a polyethylene AS obtained by the Rumanian polymerization procedure with amyl sodium [42].

Figure II-14 shows the comparison between the γCH_2 regions of four polyethylenes with various degrees of crystallinity [44]. It can be seen that an increased degree of crystallinity results in a decrease in the apparent

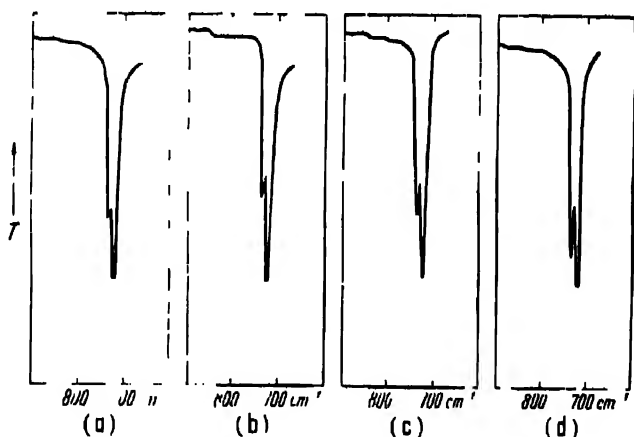


Fig. II-14 γCH_2 bands in polyethylenes of various degrees of crystallinity:

(a) ICI, 80%; (b) AS, 85%; (c) Hostalen, 80%; (d) Marlex, 95%.

intensity ratio of the two bands. A decrease in crystallinity could be demonstrated in thermally degraded polyethylenes AS, the random structure being favored at high temperatures [42]. Oxidative degradation has an opposite effect and the intensity of the 730 cm^{-1} band increases.

Studies of long chain hydrocarbons by polarized radiations showed the different behavior of the two branches of the $721 - 730\text{ cm}^{-1}$ doublet [43, 44]. In hexatriacontane crystals (C_{36}) the 730 cm^{-1} band shows parallel dichroism, while the 721 cm^{-1} band shows perpendicular dichroism. In polyethylene it is possible to evaluate from the dichroic ratio of the $721 - 730\text{ cm}^{-1}$ doublet both the degree of crystallinity [26] and the orientation of the crystalline region in films prepared by extrusion and subsequent stretching [30].

Figure II-15 shows the $700 - 750\text{ cm}^{-1}$ region of spectra recorded with polarized light in the case of a polyethylene film after extrusion (Fig. II-15a) and after 200% stretching (Fig. II-15b) [30]. The same bands were used to determine the degree of crystallinity in copolymers of ethylene-propylene [44] as well as other polymers.

Out of plane twisting and wagging vibrations of the CH_2 group (Fig. II-3e, f). The calculated frequencies for these vibrations are $1150 - 1350\text{ cm}^{-1}$ [1]. These vibration modes are affected by molecular structure and in general

give rise to low intensity bands. For this reason they are of little analytical value.

The band arising almost constantly at $1303\text{--}1307\text{ cm}^{-1}$ in *n*-alkanes is assigned to the out-of-plane wagging vibration δCH_2w . In lower members, bands at slightly higher frequencies were observed (1336 cm^{-1} in propane and 1350 cm^{-1} in crystalline *n*-butane). However, these assignments are not

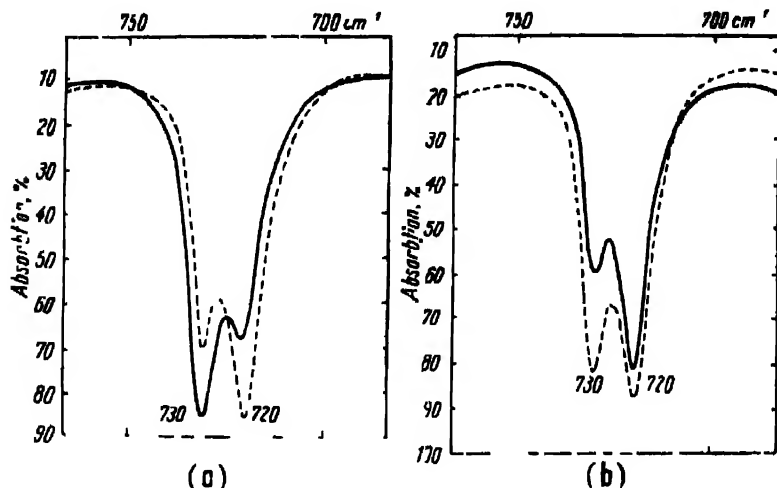


Fig. 11-15 Dichroism of the γCH_2 band in polyethylene.

(a) after extrusion; (b) after 200% stretching. The dotted line represents the spectrum recorded with radiations in which the plane of polarization is parallel to the extrusion and the stretching directions, respectively. The solid line represents the spectrum recorded with radiations with a polarization plane perpendicular to this direction [30]

fully substantiated because not enough is known about the degree of coupling of these vibrational modes with skeletal vibrations having the same symmetry [1]. Spectra of higher straight chain alkanes recorded in the solid state show a series of equidistant bands in the $1150\text{--}1350\text{ cm}^{-1}$ region; the number and intensity of these bands increase steadily with the number of carbon atoms in the chain. In *n*-octadecane the bands arise at $1160\text{--}1340\text{ cm}^{-1}$ [45]. The six bands of tetradecane in the $1187\text{--}1305\text{ cm}^{-1}$ region are also assigned to the out-of-plane C-H vibration coupled with skeletal vibrations.

The existence of a progression in the number of bands due to interaction of vibrations arising from adjacent CH_2 groups was predicted on theoretical grounds as well [46]. They can arise from more complex vibrations with participation not only of molecular interactions, but also of vibrations of the crystalline lattice. Functional groups at the end of a long paraffinic chain do not alter the absorption pattern of the hydrocarbon residue in this region. Figures 11-16 and 11-17 show such progressions of bands [47] in

INFRARED SPECTRA OF ORGANIC COMPOUNDS

hexadecanol and octadecanol, as well as in a series of higher carboxylic acids. As in the case of bands assigned to the γCH_2 vibrational mode, these bands show a strong dichroism.

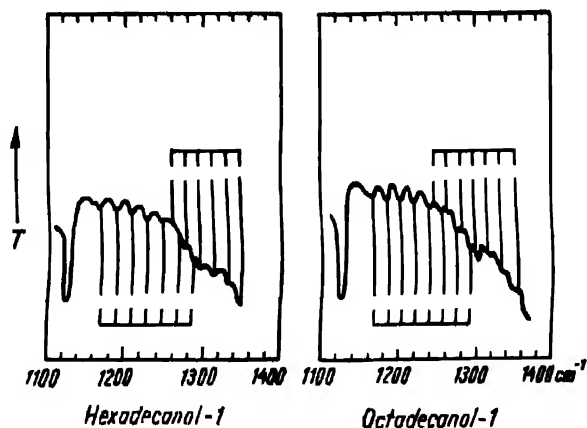


Fig. II-16 Progression of δCH_2 and δCH_2 bands in spectra of some long chain polymethylenic compounds in the solid state [47].

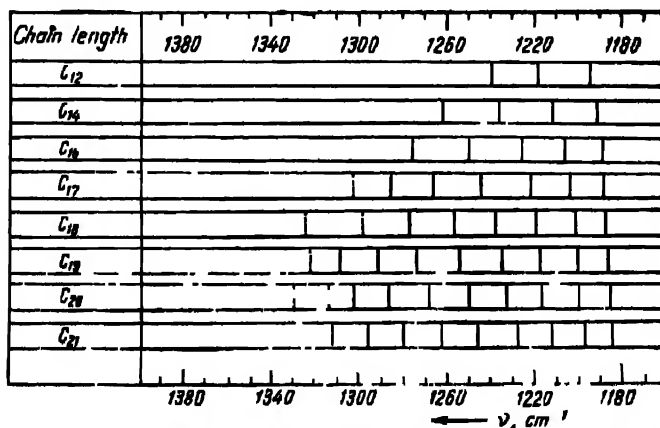


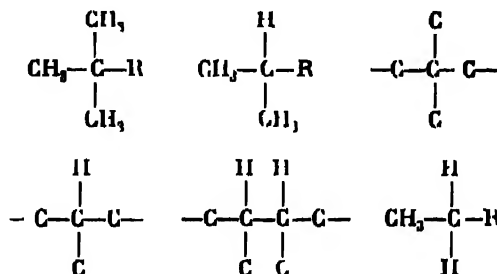
Fig. II-17 Progressions of bands in infrared spectra of long chain carboxylic acids in the solid state. The number of bands increases with chain length [47].

b. Isoalkanes or isoparaffins

Spectra of isoalkanes differ from those of straight chain alkanes in the 750–1500 cm^{-1} region. The characteristic aspects are due to C–C stretching modes, to skeletal modes, and deformation modes of C–H linkages of methyl and methylene groups. Vibrations arising from the tertiary C–H linkage are

present as well. The three vibrational modes of this linkage are shown in Fig. II-2. Generally speaking, the >C-H stretching mode is difficult to identify. A very weak band around 2890 cm^{-1} is assigned to this mode [19]. Deformation vibrations (Fig. II-2b and c) of the >C-H linkage are doubly degenerate in symmetrical molecules (e.g., in isobutane), giving rise to a single absorption at about 1335 cm^{-1} . In molecules with less symmetrical structures the band can be split into a doublet between 1330 and 1360 cm^{-1} . Since this region is extremely close to the deformation mode of the CH_3 group, the absorption of the tertiary C-H group is usually very difficult to identify.

Branched hydrocarbons with one or two methyl groups attached to the same carbon atom, either terminal or internal, have been studied more systematically [48, 49]. Some representative structures are shown below:



Although there is no general agreement on exact assignments of all frequencies, particularly the skeletal ones [48], some bands are of value in identification of various types of branching.

a. Isoalkanes with *t*-butyl groups $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{R} \\ | \\ \text{CH}_3 \end{array}$ The *t*-butyl group behaves

like a rigid entity. Its three-fold symmetry precludes rotational isomerism. Rotational isomers observed in branched hydrocarbons with *t*-butyl groups arise from the hydrocarbon group R attached to it.

The first member of the isoalkane series containing a *t*-butyl group is neopentane. Though assignments of vibrations in neopentane and deuterio-neopentane [48] are not conclusive, some characteristic frequencies for the *t*-butyl group could be pointed out.

Several CH_3 groups when attached to the same carbon atom give rise to a characteristic splitting of the band because of the symmetric deformation mode of the methyl group, which in normal alkanes appears at 1380 cm^{-1} . In structures with *t*-butyl groups, two bands arise with mean frequencies at 1397 ± 5 and $1370 \pm 3\text{ cm}^{-1}$.

Of great practical value for the identification of the *t*-butyl group are two strong bands in the infrared (and Raman) at about 1250 and 1210 cm^{-1} . These bands certainly arise from the splitting of the 1249 cm^{-1} band in neopentane, which is considered to be either a skeletal vibration or an in-phase rocking of the *t*-butyl group [18] (Table II-5).

Table II-5 Characteristic frequencies (cm^{-1}) in isomknes with *t*-butyl groups ($(\text{C}_4\text{H}_9)_3\text{C}-\text{R}$ [48])

| Hydrocarbon | $\nu\text{C}-\text{C}$ or CH_2 | | | $\nu\text{C}-\text{C}$ |
|-----------------------------|---|-------|------|------------------------|
| 2,2-dimethylbutane | 1252s | 1217s | 929m | 711w |
| 2,2-dimethylpentane | 1250 | 1209 | 926 | 741 |
| 2,2-dimethylhexane | 1250 | 1202 | 932 | -- |
| 2,2,3-trimethylbutane | 1252 | 1212 | 927 | 686 |
| 2,2,3-trimethylpentane | 1244 | 1218 | 928 | 716 |
| 2,2-dimethyl-3-ethylpentane | 1218 | 1218 | 919 | 729 |

* In the liquid state: *s* — strong; *w* — weak; *m* — medium.

It must be pointed out that the 1250 cm^{-1} band is constant in position when R is changing. The 1210 cm^{-1} band varies. Generally speaking, its frequency decreases when the mass of the R group increases. In compounds with branched R groups, the decrease in frequency is smaller when the branching is closer to the *t*-butyl group. The relative intensity of the two bands depends to a large extent on the structure of the molecule in the vicinity of the *t*-butyl group. Generally speaking, the intensity of the 1250 cm^{-1} band is higher. However, if the R group is branched in the vicinity of the *t*-butyl group, the 1250 cm^{-1} band is weaker than that at 1210 cm^{-1} . The low intensity band arising at 930 cm^{-1} cannot be used for the identification of the *t*-butyl group because of bands of similar intensities arising in this region from other alkanes.

b. **Isomknes with isopropyl groups** $(\text{CH}_3)_2\text{CH}-\text{R}$. Isobutane is the first member of this series ($\text{R} = \text{CH}_3$). The isobutane molecule has been thoroughly investigated [18]. Contrary to the *t*-butyl group, the isopropyl group is not symmetrical and even in the simplest case of 2-methylbutane, conformational isomers arise in solution. In these isomers the isopropyl group makes the spectrum more complicated.

The presence of the isopropyl group causes a splitting of the band arising from the symmetrical deformation mode of the methyl group. The high frequency component of the doublet arises at 1380 - 1385 cm^{-1} and the low frequency one at 1366 - 1372 cm^{-1} . The band at 1370 cm^{-1} is of value for the identification of the group, even if the other component of the doublet at about 1380 cm^{-1} is obscured by absorptions due to other methyl groups in the molecule.

Of great value for the identification of the group is the lower frequency band at 1170 cm^{-1} (Table II-6). This medium or high intensity band is sensi-

Table II-6 Characteristic frequencies (cm^{-1}) in isoalkanes* with isopropyl groups $(\text{CH}_3)_2\text{CH}-\text{R}$ [48]

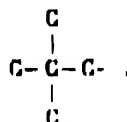
| Hydrocarbon | $\nu\text{C}-\text{C}$ or νCH_3 | | | $\nu\text{C}-\text{C}$ |
|--------------------|--|------|-----|------------------------|
| 2-methylbutane | 1176 | 1149 | 920 | 974 |
| 2-methylpentane | 1172 | 1147 | 920 | 816 |
| 2-methylhexane | 1171 | 1145 | 918 | 822 |
| 2-methyloctane | 1171 | 1144 | 919 | 824 |
| 2,3-dimethylbutane | | 1153 | 921 | |

* In the liquid state.

tive to structural changes in the hydrocarbon group R. Undoubtedly it corresponds to the 1170 cm^{-1} band in the spectrum of isobutane. The band at $\sim 955\text{ cm}^{-1}$ of variable intensity and the strong band at 920 cm^{-1} occurring in compounds with isopropyl groups are of limited value for the identification of these groups because of absorptions arising in the same region from compounds with *t*-butyl groups and many other alkanes.

The isoalkanes with two isopropyl groups give rise to the same bands as those with one group. In these compounds, for example, in 2,3-dimethylbutane, conformational isomers can be observed [18].

c. Isoalkanes with an internal quaternary carbon atom



These isoalkanes contain the structural unit C_q , which has some analogies with the *t*-butyl group.

The band arising from the symmetrical deformation mode of the CH_3 group shows the characteristic splitting into a doublet at 1384 and 1367 cm^{-1} .

Compounds of this structure have two additional strong bands 1210 cm^{-1} and 1190 cm^{-1} . The latter has a constant frequency and, being the strongest one in this region, is of value for the identification of structures with a quaternary carbon atom (Table II-7).

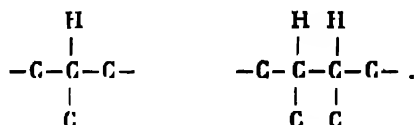
Table II-7 Characteristic frequencies (cm^{-1}) of isoalkanes with a quaternary carbon atom*

| Hydrocarbon | $\nu\text{C}-\text{C}$ or CH_3 | | | $\nu\text{C}-\text{C}$ |
|-------------------------|---|------|------|------------------------|
| 3,3-dimethylpentane | 1217 | 1192 | 1000 | 695 |
| 3,3-dimethylhexane | 1212 | 1189 | 1006 | 725 |
| 2,2,3-trimethylpentane | 1211 | 1188 | 1005 | 672 |
| 3-ethyl-3-methylpentane | 1232 | 1179 | 1016 | 686 |

In the liquid state.

The band arising at $1000-1010\text{ cm}^{-1}$ is particularly strong in structures with a quaternary carbon atom and an ethyl group. The low frequency region (below 900 cm^{-1}) is too complicated to be of value for identification purposes [48].

d. **Isalkanes with internal tertiary carbon atoms.** These compounds have the unit C_4 which has some analogies with the isopropyl group:



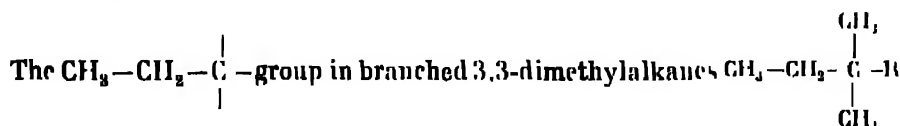
Interpretation of spectra based on comparison between the two types of compounds is difficult because of coupling of vibrations arising from this group with those arising from the rest of the molecule and because of the existence of rotational isomers in spectra recorded in solution or in the liquid state [2]. Some characteristic bands in spectra of these compounds are shown in Table II-8 [48].

Table II-8 Characteristic frequencies (cm^{-1}) in isalkanes with tertiary carbon atoms* [48]

| Hydrocarbon | $\nu\text{C}-\text{C}$ or $\nu\text{C.H}_2$ | | $\nu\text{C}-\text{C}$ |
|----------------------|---|------|------------------------|
| 3-methylpentane | 1155 | 1043 | 1015 |
| 3-methylhexane | 1155 | 1032 | 1002 |
| 3-methylheptane | 1155 | | 1011 |
| 3-methyloctane | 1155 | 1019 | 1012 |
| 3-ethylpentane | 1155 | 1050 | 1005 |
| 3-ethylhexane | 1155 | 1043 | 1011 |
| 2,3-dimethylbutane | 1129 | 1066 | 921 |
| 2,3-dimethylhexane | 1127 | 1075 | 919 |
| 3,4-dimethylhexane** | 1122 | 1071 | |
| 4,5-dimethyloctane | 1124 | 1077 | 910 |

* In the liquid state

** Absorbs at 1160 cm^{-1}



3. Cyclic saturated hydrocarbons

Cyclic saturated hydrocarbons (cycloalkanes or monocyclic cycloparaffins) have rings with $n \geq 3$ methylene groups. Bi- and polycyclic compounds with fused rings can formally be considered as arising from monocyclic compounds by bridging of two or several carbon atoms.

Besides stretching and deformation vibrations of C—H linkages, skeletal C—C vibrations which could give rise to characteristic vibrations dependent on ring size have to be considered as well. The different nature of covalent bonds in these rings, as well as a number of steric factors are the most important elements in assignments of characteristic frequencies in cycloalkanes. There are important differences between strained three- and four-membered rings with abnormal linkages and larger strain-free rings. For this reason, strain-free cycloalkanes and small-ring cycloalkanes (C_3 , C_4) are described separately. Medium-sized rings C_5 — C_{11} show some special features because of the proximity of CH_2 groups imposed by the geometry of the molecule. The spectra of cycloalkanes with large rings, above 12 carbon atoms, are similar to those of straight-chain alkanes. Bi- and polycyclic compounds show some special features and will be treated separately.

a. Strain-free cycloalkanes

In strain-free rings, carbon atoms do not show appreciable deviation from the sp^3 hybridization of straight-chain alkanes. Steric factors are mainly responsible for shifts in frequency.

a. C-H stretching mode. In five- and six membered rings, stretching modes of the CH_2 groups give rise to the same frequencies as in acyclic saturated hydrocarbons.

The symmetrical stretching mode of methylene groups in cyclohexane has a frequency of 2854 cm^{-1} and the asymmetrical mode, of 2927 cm^{-1} [50]. In cyclopentene the νCH_2 asym band arises at a higher frequency (2967 cm^{-1}), while the νCH_2 sym band is closer to the average position (2878 cm^{-1}). In the same region a number of secondary bands complete the characteristic pattern of each hydrocarbon. Thus the spectrum of cyclopentane shows a weak band at 2933 cm^{-1} assigned to a resonance with the overtone of the scissoring mode of the methylene group [51]. In liquid films, cyclohexane and cyclooctane show a number of absorptions with less than medium intensity in the 2600 — 2800 cm^{-1} region [50—52]. Figure II-18 shows the 2500 — 3000 cm^{-1} region in infrared spectra of cycloalkanes with 5, 6, and 8 carbon atoms.

In alkylcyclopentanes the νCH_2 asym band overlaps with the νCH_2 asym band of the side chains. The bands at 2800 — 3000 cm^{-1} have been used in quantitative analysis of cycloparaffins in mixtures with straight chain alkanes [53, 54].

In medium-sized rings transannular interactions are observed [55--57]; for example, in cyclodecanol the distance between hydrogen atoms inside the ring is 1.8 \AA [55, 57] and the frequency of the C—H vibrations of the respective bands rises to 2991 cm^{-1} . In the twelve-membered ring, in which the transannular H—H distance is 2 \AA , no change in C—H bond frequencies is observed.

Large rings can be considered as two chains of straight-chain alkanes with *trans* zigzag configuration having joined ends. Along with other physical and

chemical properties, the spectra of these cycloalkanes are similar to those of straight-chain alkanes.

b. **C-H deformation modes.** The most characteristic vibration of the CH_2 group is the scissoring mode. Its absorption arises in the same uncrowded region as in *n*-alkanes (Fig. 11-19).

In cyclohexane and cyclopentane, the frequency of this vibration is slightly lower than the 1468 cm^{-1} band in straight-chain alkanes. Cyclohexane has

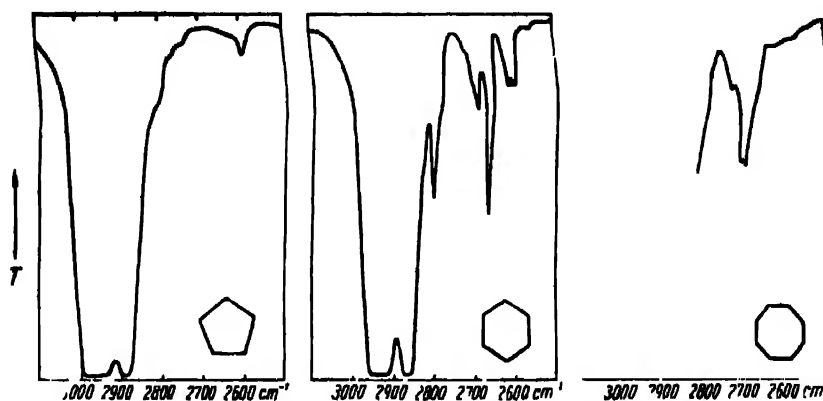


Fig. 11-18 Infrared spectra of some cycloalkanes in the $2500\text{--}3000\text{ cm}^{-1}$ region (combination and fundamental CH bands)

a single band at 1450 cm^{-1} and cyclopentane at 1455 cm^{-1} . Because of this decrease in frequency in alkylcycloparaffins, the band arising from the scissoring mode of the ring methylene group differs in position from the 1460 cm^{-1}

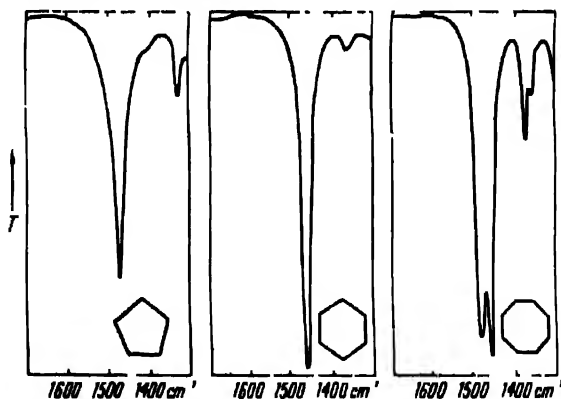


Fig. 11-19 Infrared spectra of some cycloparaffins in the region of C-H deformation modes.

band arising from the asymmetric deformation mode of the side chain CH_3 group. In methylcyclohexane the frequency of the δCH_3 band is 1452 cm^{-1} , while the δCH_2 asym band arises at 1466 cm^{-1} .

In ethylcyclohexane the vibration of the side chain CH_2 group cannot be identified. While the ring δCH_2 band remains constant at 1452 cm^{-1} , the 1464 cm^{-1} band contains both the δCH_2 and the δCH_3 absorptions.

In more complicated structures, for example in steroid hydrocarbons, the spectrum in the $1300\text{--}1500\text{ cm}^{-1}$ region is more complex. In many instances, however, it is possible to identify characteristic bands of various deformation modes arising from CH_2 and CH_3 groups in rings or side chains [51].

In medium- and large-ring cycloparaffins, two or three bands arise in this region, depending on ring size (see Table II-9). The maximum difference (Δ_{max}) is $10\text{--}43\text{ cm}^{-1}$.

Table II-9 Frequency of the δCH_2 deformation modes in cycloparaffins [58]

| Hydrocarbon | Number of atoms in the ring | δCH_2 , cm^{-1} | | Δ_{max} , cm^{-1} |
|------------------|-----------------------------|--|------|--|
| Cyclopentane | 5 | 1455 | — | — |
| Cyclohexane | 6 | 1450 | — | — |
| Cycloheptane | 7 | 1464 | 1453 | 11 |
| Cyclooctane | 8 | 1477 | 1470 | 27 |
| Cyclononane | 9 | 1487 | 1469 | 43 |
| Cyclodecane | 10 | 1483 | 1454 | 33 |
| Cyclododecane | 12 | 1470 | 1447 | 23 |
| Cyclotridecane | 13 | 1461 | 1447 | 14 |
| Cyclotetradecane | 14 | 1463 | 1446 | 17 |
| Cyclopentadecane | 15 | 1460 | 1449 | 11 |
| Cyclohexadecane | 16 | 1461 | 1448 | 13 |
| Cycloheptadecane | 17 | 1460 | 1450 | 10 |

The multiplicity of δCH_2 bands in some cycloparaffins was attributed to conformational effects. Depending on their arrangement in space several vibrational types of methylene groups can exist. In cyclopentane and cyclohexane all CH_2 groups are equivalent because all of them have a relatively equivalent orientation. Their spectra have a single band arising from the δCH_2 mode. In medium and large rings, CH_2 groups can be oriented in such a way as to become nonequivalent with respect to their relative positions. Some can be farther apart, others can be closer together. Vibrational interaction of the latter will obviously modify the deformation frequency. In spectra of medium- and large-ring cycloparaffins, two or three absorptions in the $1413\text{--}1487\text{ cm}^{-1}$ were indeed observed. Based on these observations the following rule was proposed [58]: a molecule with x distinct δCH_2 bands has at least x types of CH_2 groups; this differentiation is due to neighboring effects.

c. **Ring vibrations.** Many papers point out the constant appearance of absorption bands at $680\text{--}1260\text{ cm}^{-1}$ in spectra of compounds containing rings of various sizes. These absorptions were assigned to characteristic ring vibrations.

In cyclopentane and in compounds with cyclopentane rings, bands arising at 900 cm^{-1} [59] or 930 and 977 cm^{-1} [60,61] are mentioned. The 950 cm^{-1}

band in the spectrum of cyclopentane was assigned to the C—C stretching vibration [62]. In substituted cyclohexanes the following bands are mentioned: 860—890 cm^{-1} [51, 59, 61, 63] or 952—1000 cm^{-1} and 1000—1055 cm^{-1} [60].

In cycloheptane ring vibrations are believed to occur at 960 cm^{-1} [64] and in cyclooctane at 703 cm^{-1} [61]. However, a critical review of absorptions of cycloparaffins in this region points out the absence of reliable correlations between bands and ring size [65] (see also "Strained Cycloparaffins").

d. Conformation of cycloalkanes. In the classical configuration of a cycloalkane the atoms can be oriented in space in several ways due to restricted rotation about simple C—C bonds. Each of the resulting *conformational isomers* is a distinct molecular species [66]. Being dynamic systems with a finite number of conformational possibilities, the cycloalkanes will adopt (under normal conditions) forms corresponding to the lowest values of the potential curves. The potential barrier between various conformational isomers is low and at normal temperature their interconversion occurs readily, reaching an equilibrium. The ratio of isomers at equilibrium is temperature dependent. In many instances only one conformer is present, the other ones being energetically unstable. A useful method for establishing conformational homogeneity or heterogeneity is the study of spectra at various temperatures.

When a system contains appreciable concentrations of two or more conformers in dynamic equilibrium, these conformers can be detected by infrared spectra (see "Cyclopentane"). The majority of basic cycloalkanes have been studied from this point of view. The results of these studies are as

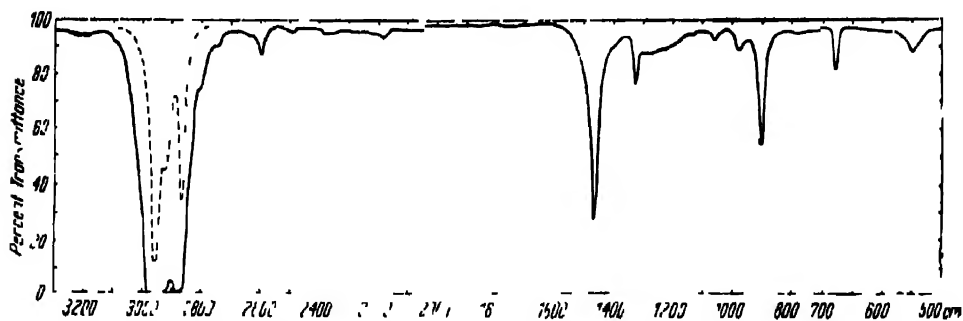


Fig. II-20 The infrared spectrum of cyclopentane. Solid line — liquid film; dotted line — dilute solution in CCl_4 .

reliable as those obtained by other physical methods (electron diffraction, X-rays, nuclear magnetic resonance).

1. *Cyclopentane.* The conformation of cyclopentane has been studied by a great number of physical methods. The classical planar pentagonal configuration belongs to the symmetry class D_{5h} . In this model the five CH_2 groups should be eclipsed. Vibrational spectra of cyclopentane (infrared, Raman) do not exactly fit this model (Fig. II-20).

There are differences between frequencies calculated on the basis of the planar model D_{5h} (Table II-10) and the experimental values, mainly in the region of C—C skeletal vibrations [62].

Table II-10 Calculated frequencies for cyclopentane with D_{5h} symmetry [62]

| Type of vibration | Activity of different species | Active in R | | | Active in IR | | Inactive | | |
|---------------------------|-------------------------------|-------------|--------|---------|--------------|--------|----------|--------|--------|
| | | A'_1 | E'_2 | E''_2 | A''_2 | E'_1 | A'_2 | A'_1 | E'_2 |
| δCH_2 | | 1450 | 1452 | | | 1440 | — | — | — |
| $\delta CH_2 t$ | | — | — | 1348 | | — | — | 1295 | 1327 |
| $\delta CH_2 w$ | | | 1207 | | | 1298 | 1231 | — | — |
| $\gamma CH_2 r$ | | | | 905 | 896 | — | — | — | 1020 |
| $\nu C-C$ | | 831 | 1409 | — | — | 951 | — | — | — |
| Deform. $\widehat{C-C-C}$ | | | 549 | — | — | — | — | — | — |

The discrepancy between experimental values and those calculated for the D_{5h} symmetry could not be explained on the basis of a nonplanar regular pentagonal model with a single out-of-plane carbon atom [67]. Rather the infrared spectrum corresponds to a mixture of several conformational isomers of about equal stability, resulting from a twisting of CH_2 groups about the C—C bond. The resulting model is that of a nonplanar pentagon with a carbon atom alternately bent by 0.2\AA out of a plane passing through the other four carbon atoms.

2. *Cyclohexane*. Electron diffraction has shown [68] that under normal conditions cyclohexane has a chair conformation (1) (Fig. 11-21) with D_{3d} symmetry. The electron diffraction data do not exclude, however, a minor contribution of the less symmetrical boat form (2) (Fig. 11-21).

Table II-11 Observed and calculated frequencies in cyclopentane [62]

| Vibration type | ν observed cm^{-1} | ν calculated (D_{5h}) cm^{-1} |
|---------------------------|---------------------------------|--|
| δCH_2 | 1462 | 1449 |
| $\delta CH_2 t$ | 1376 | 1298 |
| | 1317 | — |
| $\delta CH_2 w$ | 1250 | 896 |
| | 950 | — |
| $\gamma CH_2 r$ | 895 | 951 |
| | 950 | — |
| $\nu C-C$ | 827 | — |
| | 769 | — |
| Deform. $\widehat{C-C-C}$ | 616 | — |
| | 547 | — |

In the lower energy, more stable chair conformation, all the CH_2 groups are staggered. The Raman spectrum [69] fits the D_{3d} model but at higher temperatures a dynamic equilibrium between the two forms (1) and (2) is not excluded [70]. The vibration modes of the cyclohexane ring in the chair

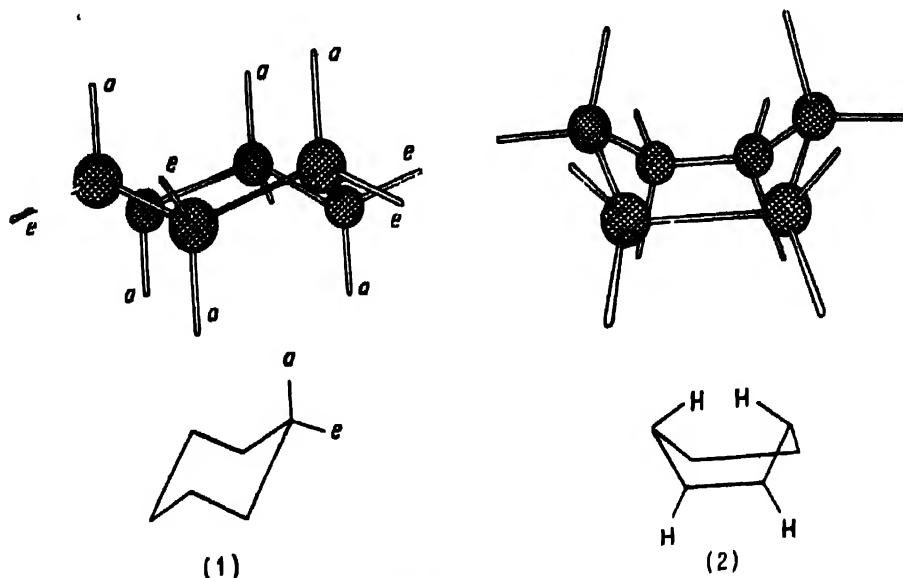


Fig. II-21 Conformations of cyclohexane: (a) axial bonds; (e) equatorial bonds.

form (D_{3d} symmetry) are shown in Fig. II-22 [71, 72]. The coordinates and numbering are adapted from data for the six-membered ring [73]. The deformation modes of cyclohexane are shown in Fig. II-23. In the chair conformation, six out of twelve C—H bonds are approximately parallel to the trigonal symmetry axis of the molecule (*axial* or *polar* bonds). The remaining six bonds are approximately parallel to the horizontal plane of the ring and

are known as *equatorial bonds*. In vibrational spectra the two types of bonds cannot be differentiated. They give rise to a single absorption at 1450 cm^{-1} .

Table II-12 Assignment of bands in the infrared spectrum of cyclohexane [72]

| Frequency, cm^{-1} | Vibration type |
|-----------------------------|------------------------|
| 522 | Deform. C-C |
| 864 | $\nu\text{C-C}$ |
| 903 | $\gamma\text{CH}_2, r$ |
| 1030 | $\gamma\text{CH}_2, r$ |
| 1261 | $\delta\text{CH}_2, w$ |
| 1348 | $\delta\text{CH}_2, t$ |
| 1456 | δCH_2 |
| 2854 | νCH_2 sym |
| 2927 | νCH_2 asym |

The assignment of bands in the infrared spectrum of cyclohexane (Fig. II-24) is shown in Table II-12 [70, 72, 74-76].

In monosubstituted derivatives of cyclohexane, the substituent can be either in an axial or an equatorial position. Conformations with equatorial substituents are energetically favored. In some alkylcyclohexanes the conformational heterogeneity could be pointed out by infrared spectra [70].

The axial or equatorial orientation of substituents can be clearly demonstrated in compounds with polar substituents, halides, haloketones, and alcohols (see below).

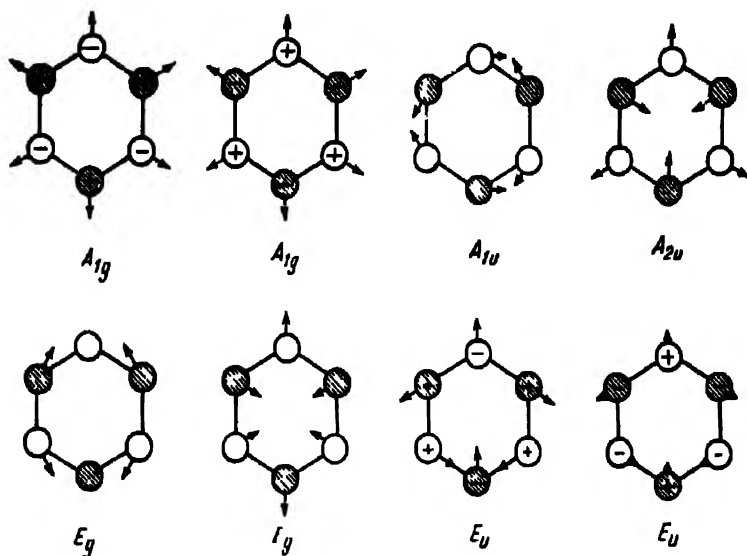
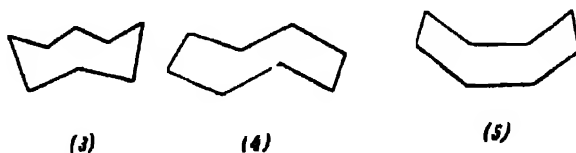


Fig 11-22 Vibration modes of the cyclohexane ring in the chair form (D_{3d} symmetry). The atoms above the plane of the drawing are represented by hatched circles; those below by white circles. For each degenerate mode only one of the two component vibrations is represented [72].

3. *Cyclooctane*. Three conformations (3), (4), and (5) have been proposed for the eight-membered ring [57, 77–79];



(3) and (5) are more probable. The constant number of bands observed in infrared spectra of cyclooctane at various temperatures [77, 78] leads to the conclusion that it exists mainly in one conformation. The *crown conformation* (3) has three different types of CH_2 groups, differentiated by neighboring effects; conformations (4) and (5) have two types of CH_2 groups. The infrared spectrum of cyclooctane (Fig. 11-25) shows three δCH_2 bands arising at 1477, 1470, and 1450 cm^{-1} (3); therefore it was concluded that the crown (3) conformation is the most probable one. This conclusion is also supported by the fact that cyclooctane exhibits transannular interactions.

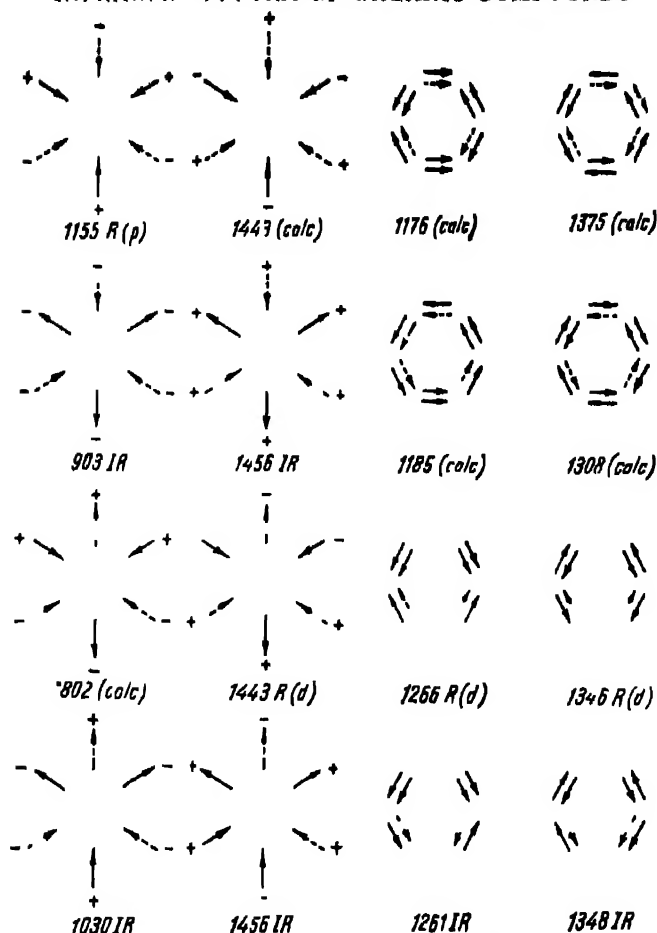


Fig. II-23 C-H deformation modes in the chair form of cyclohexane (D_{3d} symmetry). The peripheral symbols show motions of equatorial hydrogens; the internal symbols, those of axial hydrogens. The internal solid arrows show the motion of hydrogens above the plane of the drawing; the dotted arrows show the motion of hydrogens below this plane. The numbers represent frequencies in cm^{-1} .

(*R*) active in Raman, (*p*) polarized, (*d*) depolarized (*IR*) active in the infrared.

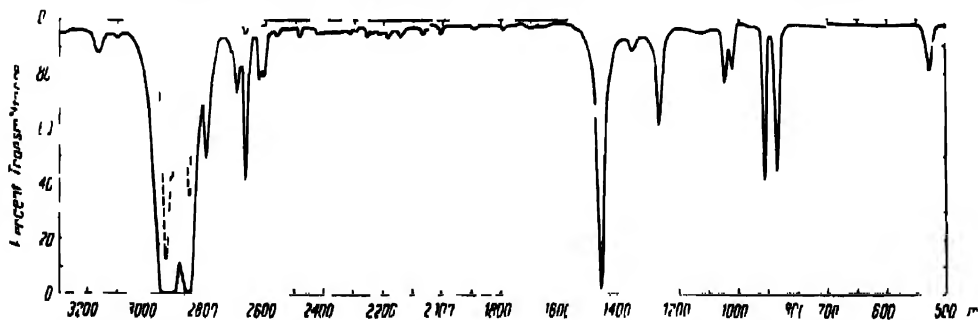
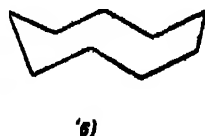


Fig. II-24 Infrared spectrum of cyclohexane.

4. *Cyclononane*. A number of geometrical models have been proposed for the cyclononane molecule [80, 81]. Those with C_3 or C_3 symmetry should have five types of CH_2 groups whereas those with C_3 symmetry (6) should have three types of CH_2 groups. The infrared spectrum of cyclononane shows three bands δCH_2 arising at 1487, 1469, and 1444 cm^{-1} [58]. This favors conformation (6) which belongs to the point group C_3 .



5. *Cyclodecane*. The conformation of the ten-membered ring was widely discussed because of the low reactivity of the carbonyl group in cyclodeca-

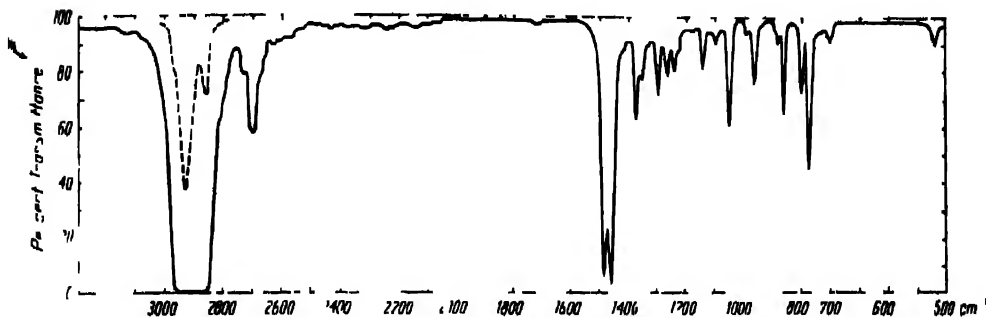
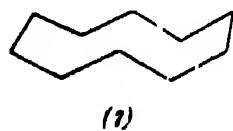


Fig 11-25 Infrared spectrum of cyclooctane.

none [57]. Molecular models with C_{2h} or C_{2v} symmetry seem more probable, since they are in agreement with the properties of this system [80]. However, other possible conformations cannot be excluded. Structure (7) with three types of CH_2 groups is supported by infrared data (three δCH_2 bands at 1483, 1454, and 1445 cm^{-1}) [58] and is in agreement with the X-ray analysis as well [82]. In cyclodecanol the transannular interaction of the methylene groups increases the νCH_2 frequency, by an appreciable amount and the corresponding band arises at 2991 cm^{-1} [52].



6. *Cyclododecane*. The structure of cyclododecane was the first one among cycloalkanes to be established by X-ray analysis [83]. The infrared spectrum (two δCH_2 bands at 1470 and 1447 cm^{-1}) supports the existence of two types of CH_2 groups, possible in structures with D_{2d} symmetry [58]. This conformation explains the properties of the carbonyl group in cyclododecanone, which can adopt a sterically nonhindered position [57].

7. *Large rings*. Rings containing more than 12 carbon atoms can be visualized as two connected parallel chains of *n*-alkanes with *trans* zigzag conformation. The distance of 4.45 Å between chains (determined by X-ray analysis) corresponds to the distance between chains in a crystal of a straight-chain alkane. Spectra of cycloalkanes with 12–17 carbon atoms show two δCH_2 bands arising at 1460–1463 cm^{-1} and at 1446–1450 cm^{-1} [58]. The distance

between the maxima of these bands (see Table II-9) is slightly larger in even-numbered carbon atom rings than in odd-numbered ones.

b. Cycloalkanes with strained rings

In normal, medium, or large ring cycloalkanes, the distortion of the normal bond angles of the carbon atoms is negligible. In these molecules chemical bonds are formed according to the principle of maximum orbital overlap and the hybridization, sp^3 , is the same as in n -alkanes.

In small ring cycloalkanes (C_3 , C_4) the distortion of the two orbitals of the ring carbons (to 60° -equilateral triangle in cyclopropane and 90° -square in cyclobutane) would result in considerable strain. However, the energy content of these molecules, although increased by comparison with the other cycloalkanes, does not support these models. It was shown that an energetically more favorable arrangement is achieved if one assumes that the two orbitals of the C - C bond form an angle θ with the line connecting these two atoms [84]. The calculated value of angle θ is 22° in cyclopropane and 9° in cyclobutane. Such an orientation imposes a deviation from the principle of maximum orbital overlap but the decrease in ring strain makes the system more stable. These bonds are of a special type; they are somewhat bent (banana-shaped; Fig. II-26 and II-27).

In this model [84] the orbitals no longer have an sp^3 hybridization in which the s/p ratio is $1/3$. The C—C bonds have more p character, while the C—H bonds have more s character. The s character of C—H bonds in cyclopropane is thought to be 32%; In cyclobutane the s character to 27% [85]. The increase in s component in the hybrid orbital of the C—H bond increases the force constant and thus the vibration frequency. In cyclopropane the ν_{CH} frequency is greater than 3000 cm^{-1} , approaching values of C—H frequencies for sp^2 hybridized carbon atoms (alkenes, aromatic hydrocarbons).

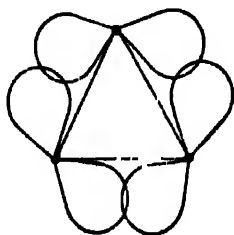


Fig. II-26 C—C orbitals in cyclopropane.

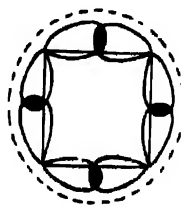


Fig. II-27 C—C orbitals in cyclobutane.

a. **Cyclopropane.** Electron diffraction data show [86] that in the model corresponding to the cyclopropane structure the three carbon atoms are at one corners of an equilateral triangle and the C—H bonds are in median planes perpendicular to the plane of the triangle. Such a system belongs to the point group D_{3h} [87]. The calculated normal vibration modes for cyclopropane

with D_{3h} symmetry agree with experimental data obtained in the infrared in the liquid and gaseous states [85–88]. In the crystalline state (orthorhombic, C_{2v} or D_{2h} symmetry), the molecules are in a lattice with C_2 symmetry [89].

Of the 21 normal vibration modes of cyclopropane (with D_{3h} symmetry) 14 are doubly degenerate, resulting in 14 distinct frequencies [89]. The distribution of vibration modes for irreducible representations of the D_{3h} symmetry (Γ) is,

$$\Gamma = 3A_1' + 1A_1' + 1A_2' + 2A_2'' + 4E' + 3E''$$

The corresponding fundamental frequencies are shown in Table II-13.

Table II-13 Frequencies (cm^{-1}) of fundamental vibration modes in cyclopropane [89]

| Vibration mode | Species | Type | Vapor | | Liquid | | Crystal | |
|----------------|---------|---------------------|-------|------|--------|------|---------|------|
| | | | R | IR | R | IR | IR | |
| ν_1 | A_1' | $\nu\text{C-H}$ | 3038 | in | 3027 | — | — | |
| ν_2 | A_1' | δCH_2 | 1454 | in | 1453 | 1453 | 1454 | |
| ν_3 | A_1' | ring | 1188 | in | 1188 | 1191 | 1194 | |
| ν_4 | A_1'' | δCH_2 | 1133* | in | 1131 | 1129 | 1133 | |
| ν_5 | A_2' | δCH_2 | in** | in | — | — | 1078 | |
| ν_6 | A_2' | $\nu\text{C-H}$ | in | 3101 | — | 3081 | 3073 | |
| ν_7 | A_2'' | γCH_2 | in | 852 | — | — | 855 | |
| ν_8 | E' | $\nu\text{C-H}$ | 3030 | 3025 | 3099 | 3013 | 3004 | |
| ν_9 | E' | δCH_2 | 1442 | 1442 | 1434 | 1432 | 1424 | 1431 |
| ν_{10} | E' | ring deformation | | 1028 | 1023 | 1026 | 1027 | |
| ν_{11} | E' | δCH_2 | 866 | 860 | 866 | 865 | 865 | |
| ν_{12} | E'' | $\nu\text{C-H}$ | 3082 | in | 3075 | | 3073 | |
| ν_{13} | E'' | δCH_2 | 1188 | in | 1178 | 1191 | 1200 | |
| ν_{14} | E'' | δCH_2 | 739 | in | 711 | 741 | 719 | |

* Forbidden.

** Inactive.

Only species A_2' and E' are active in the infrared. The four degenerate vibration modes E' correspond to C—H stretching vibrations (ν_8), deformation vibrations of the CH_2 groups (ν_9 and ν_{11}) and to the deformation vibration of the ring (ν_{10}). In spectra recorded in the vapor phase, Q branches occur at 3025, 1442, 1028, and 860 cm^{-1} [88, 90]. The spectrum of liquid cyclopropane shows broader, weaker bands at 3013, 1432, 1026, and 865 cm^{-1} . In crystals, vibrations ν_8 , ν_{10} , ν_{11} arise at 3004, 1027, and 865 cm^{-1} , and ν_9 appears as a doublet at 1434 and 1424 cm^{-1} . The A_2' modes corresponding to the C—H stretching vibration (ν_6) and the in-plane rocking of the CH_2 group (ν_7) arise at 3101 and 852 cm^{-1} (vapor, branch R). In the liquid phase ν_6 arises at 3081 cm^{-1} and is stronger, while ν_7 is totally covered by the vibration ν_{11} . In crystals, ν_6 arises at 3073 and ν_7 at 855 cm^{-1} .

b. **Compounds with cyclopropane rings.** For the characterization of compounds with cyclopropane rings, two regions have been extensively studied: 2900–3100 and 800–1100 cm^{-1} .

The region 2900–3100 cm^{-1} corresponds to stretching vibrations of ring C–H bonds. As shown above, because of the increased s character of these bonds the values of the vibration frequency are those of the C–H bonds of sp^2 hybridized carbon atoms (unsaturated compounds). The high frequency is in line with a number of special properties of cyclopropane.

Accurate assignment of absorption bands in this region depends on the resolution power of the equipment used [91]. In recordings with sodium chloride prisms the cyclopropane band arises as a shoulder on the saturated νCH vibration. Only lithium fluoride prisms could secure the complete resolution of bands. In the case of mixtures or of cyclopropanes substituted with unsaturated or aromatic groups, possible overlaps with $=\text{C}-\text{H}$ bond vibrations must be taken in account. Because of its high frequency (νCH_2 , sym = 3020 cm^{-1} , νCH_2 asym = 3085 cm^{-1}), the cyclopropane methylene group can be easily distinguished from the methylene groups of other alkanes [92].

A great number of monosubstituted derivatives of cyclopropane [92] show a band of 2995–3030 cm^{-1} , as well as a band at 3072–3099 cm^{-1} [50]. The value of these bands for the identification of three-membered rings in cyclopropane derivatives with CHR or CR_2 groups is questionable [93]. Investigation of the 2900–3100 cm^{-1} region in a great number of cyclopropane derivatives with one or all hydrogens replaced by different functional groups or in which the cyclopropane ring is part of a condensed system has shown that only 19% of the compounds absorb in the 3030–3050 cm^{-1} region [94]. The band position is affected by the substituents to such an extent that in some cases no definite conclusions with respect to the existence of a cyclopropane ring in this region can be drawn.

Some phytosterols show a band at 3030 cm^{-1} . This absorption was assigned to the stretching mode of a C–H bond in a condensed cyclopropane ring. The band arising at 3021–3058 cm^{-1} is considered characteristic for steroids and terpenes with a CH_2 group in the three membered ring. It is thus possible to differentiate compounds containing substituents at one, two, or all three carbon atoms [95].

The 800–1100 cm^{-1} region has two intervals (790–860 cm^{-1} and 1000–1020 cm^{-1}), corresponding to absorptions of the cyclopropane ring at 860 cm^{-1} (C–H deformation modes) and 1026 cm^{-1} (deformation mode of the ring). 1, 1, 3-Trimethyl- and 1, 2-dimethyl-3-ethylcyclopropane give rise to absorptions at 866 and 1026 cm^{-1} [96]. In a number of hydrocarbons with a cyclopropane ring [97], the 866 cm^{-1} band could not be identified; however, bands at 1000–1020 cm^{-1} have been observed. In 34 substituted cyclopropanes bands at 1017–1025 cm^{-1} were constantly found. They were correlated with the presence of the three-membered ring [98, 50]. Although the 1020 cm^{-1} band is present in spectra of many cyclopropanes substituted with various functional groups, some authors consider the 3000 cm^{-1} region more reliable for the identification of the three-membered ring [92]. It has been shown

that out of 42 substituted cyclopropanes, only 81% give rise to bands at $1000-1035\text{ cm}^{-1}$ and 17% at $850-870\text{ cm}^{-1}$ [94].

The possibility of utilizing bands in the $800-1100\text{ cm}^{-1}$ for identification of cyclopropane rings has been discussed by several authors [93, 94]. Although these bands arise in spectra of many compounds with cyclopropane rings, over 50% of organic compounds of various structures absorb in the same region, which makes these bands unreliable for diagnostic purposes.

c. **Cyclobutane.** Considering cyclobutane a dynamic system with finite conformational possibilities, three conformations can be examined: D_{4h} , planar (Fig. II-28a); D_{2d} , nonplanar (Fig. II-28b); and D_{2h} , planar (Fig. II-28c)

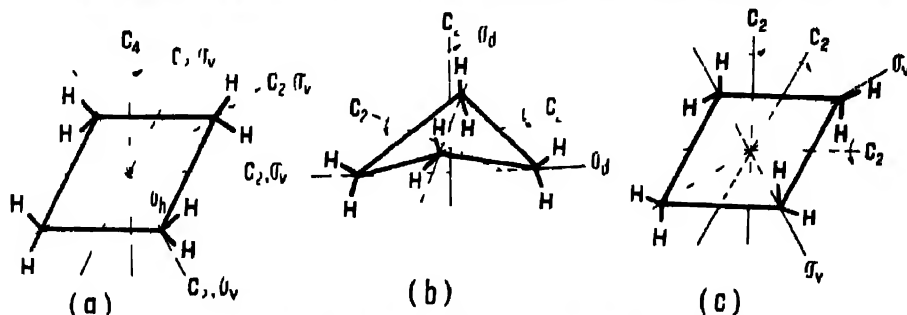


Fig. II-28 Hypothetical symmetry structures of the cyclobutane molecule: (a) D_{4h} planar; (b) D_{2d} nonplanar; (c) D_{2h} planar.

[99, 100, 105]. The planarity of the ring in the equilibrium conformation is suggested by the strain of C—C—C bonds. On the other hand, twisting about C—C bonds and transannular $C_1 - C_3$ repulsion [101] tend to give rise to a nonplanar conformation (D_{2d}).

The frequencies, symmetries, and activity of the fundamental vibration modes of cyclobutane in the two probable symmetry groups are shown in Table II-14. In any one of these groups, the Raman spectrum must be very different from the infrared spectrum.

The species D_{4h} has six fundamental vibrations active in the infrared, 11 in Raman (the rule of mutual exclusion is applied), and six inactive vibrations both in Raman and the infrared. The species D_{2d} has 12 vibration modes active in the infrared and Raman (coincident). Nine are active only in Raman and two are inactive both in Raman and the infrared.

Since the number of observed strong bands is close to that calculated for the species D_{4h} , the first spectroscopic hypothesis concerning the structure of cyclobutane predicted a planar configuration for the skeleton formed by the four carbon atoms [99].

By electron diffraction it was eventually shown that the cyclobutane ring forms a dihedral angle of 20° , but it was not possible to determine whether the ring is nonplanar, static with D_{2d} symmetry, or dynamic with D_{4h} symmetry and a strong out-of-plane deformation motion [102]. Investigation of deuterated cyclobutane has shown that vibrational spectra can be interpreted as either D_{4h} or D_{2d} symmetries [103].

Table II-14 Species and activities of fundamental vibrations in cyclobutane

| Vibration | Frequency cm ⁻¹ | Species | | Activity | | Vibration | Frequency cm ⁻¹ | Species | | Activity | |
|----------------------|-------------------------------|-----------------|-----------------|-----------------|-----------------|----------------------|-------------------------------|-----------------|-----------------|-----------------|-----------------|
| | | D _{4h} | D _{2d} | D _{4h} | D _{2d} | | | D _{4h} | D _{2d} | D _{4h} | D _{2d} |
| νCH | 2870 | A _{1g} | A ₁ | R | R | | | | | | |
| δCH_2 | 1444 | A _{1g} | A ₁ | R | R | γCH_2r | 901 | A ₁ | B ₂ | IR | IR, |
| νCC | 1003 | A _{1g} | A ₁ | R | R | | | | | | R |
| νCH | 2921 | B ₁ | A ₁ | in | R | νCH | 2980 | E _g | E | R | IR, |
| γCH_2r | (878) | B ₁ | A ₁ | in | R | | | | | | R |
| Deform. | | | | | | δCH_2t | 1220 | E _g | E | R | IR, |
| ring | (145)* | B ₁ | A ₁ | in | R | | | | | | R |
| δCH_2w | 1299 | A _{2g} | A ₂ | in | in | γCH_2r | 890 | E _g | E | R | IR, |
| δCH_2 | 1104(1155) | B ₂ | A ₂ | in | in | | | | | | R |
| δCH_2w | (1286) | B _{1g} | B ₁ | R | R | νCH | 2974 | E | E | IR | IR, |
| νCC | 928 | B _{1g} | B ₁ | R | R | | | | | | R |
| νCH_2t | 1148(1155) | A ₁ | B ₁ | in | R | δCH_2 | 1453(1420) | E | E | IR | IR, |
| νCH | 2981 | B _{2g} | B ₂ | R | IR, | | | | | | R |
| | | | | | R | δCH_2w | 1261 | E | E | IR | IR, |
| δCH | 1450 | B _{2g} | B ₂ | R | IR, | | | | | | R |
| | | | | | R | Deform. | | | | | |
| Deform. | 750 | B _{2g} | B ₂ | R | IR, | ring | 625 | E | E | IR | IR, |
| ring** | | | | | R | | | | | | R |
| νCH | 2986 | A ₂ | B ₂ | IR | IR, | | | | | | |
| | | | | | R | | | | | | |

* Out-of plane for D_{4h}; entropy measurements do not correspond to the given value

** In-plane for D_{4h}. Calculated values are given in brackets.

Discrepancy between measured entropy values [103] and those calculated for a planar model lead to attempts to interpret Raman and infrared spectra of cyclobutane as arising from a nonplanar molecule with D_{2d} symmetry [100]. This hypothesis turned out not be completely true either, because it was impossible to identify all allowed vibration modes or coincidences which should arise on loss of the center of symmetry (see Table II-15).

The authors think, however, that three coincidences (630, 750, and 1220 cm⁻¹) which do not seem to be fortuitous might point out the existence of some molecules in which one carbon atom is out of a plane passing through the other three carbons. On the other hand, changes in intensity of certain bands with temperature seem to be an additional argument in favor of the coexistence of both structures. On increasing the tem-

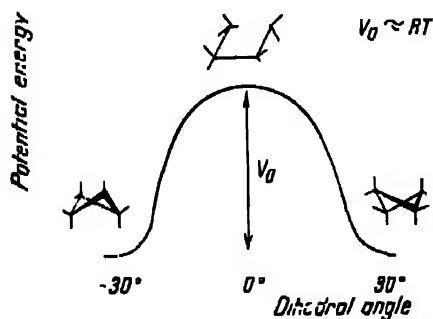


Fig. 11-29 Potential energy change with dihedral angle in the molecule of cyclobutane [105].

perature decreased intensities of bands assigned to the D_{2d} conformation (see Table II-15) are observed. The most striking modification is observed for the 750 cm⁻¹ band; its integrated absorption at 459°K was evaluated to be 73 ± 5% of the value found at 299°K. This behavior suggests

a model in which the potential energy curve for ring conversion shows two minima (Fig. II-29).

The potential barrier at normal temperature is sufficiently low for the existence of an appreciable amount of D_{4h} molecules. The 750 and 1220 cm^{-1} bands favor the hypothesis for the prevalence of the D_{2d} structure in liquid

Table II-15 Frequencies and assignments in the cyclobutane molecule [100]

| Infrared | | | | Raman | | Assignment | Species | | Activity | |
|---------------------------------------|-----------------------|---------------------------------------|----------------|---------------------------------------|----------------|---------------------|----------|----------|----------|----------|
| Gas | Liquid | | | | | | D_{2d} | D_{4h} | D_{2d} | D_{4h} |
| Pre- frequency cm^{-1} | Relative intensity | Pre- frequency cm^{-1} | Inten- sity | Pre- frequency cm^{-1} | Inten- sity | | | | | |
| 611 | | | | | | | | | | |
| 625 | 5 | 630 | 5 | 634 \pm 5 | 0.5 | Deform. ring | E | E | IR, R | IR |
| 640 | | | | | | | | | | |
| 740 | 2* | 750 | 3 | 750 \pm 5 | 1 | Deform. ring | B_2 | B_{2g} | IR, R | R |
| 758 | | | | | | | | | | |
| 901 | 10 | 907 | 10 | | | γCH_2 | B_2 | A_2 | IR, R | IR |
| | | | | 928 \pm 1 | 8 | νCC | B_1 | B_{1g} | R | R |
| | | | | 1002.6 | 10 | νCC | A_1 | A_{1g} | R | R |
| | | | | 1104 \pm 5 | 0.5 | δCH_2 | A_2 | B_2 | in | in |
| | | 1147 | 1 | 1148 \pm 5 | 2 | δCH_2 | B_1 | A_1 | R | in |
| 1210 | 2* | 1220 | 2 | 1220 \pm 1 | 5 | δCH_2 | E | F_g | IR, R | R |
| 1228 | 2 | | | | | | | | | |
| 1246 | | | | | | | | | | |
| 1261 | 10 | 1253 | 10 | | | δCH_2 | E | L | IR, R | IR |
| 1277 | | | | | | | | | | |
| 1433 | | | | | | | | | | |
| 1450 | | | | 1444 \pm 1 | | δCH_2 | B_2 | B_{2g} | IR, R | R |
| 1471 | 10** | 1445 | 10 | | | | | | | |
| 1433 | | | | | | | | | | |
| 1453 | | | | 1144 \pm 1 | 7 | δCH_2 | I | E | IR, R | IR |
| | | | | 1444 \pm 1 | | δCH_2 | A_1 | A_{1g} | R | R |
| | | | | 2870 \pm 1 | 8 | νCH | A_2 | A_{2g} | R | R |
| 2806 | 20 | | | | | νCH | B_2 | A_2 | IR, R | IR |
| | | | | 2921 \pm 3 | 7 | νCH | A_1 | B_1 | R | in |
| | | | | 2960 \pm 3 | 7 | νCH | E | E_g | IR, R | R |
| 2971 | 20 | | | | | νCH | L | F_g | IR, R | IR |
| | | | | 2981 \pm 3 | 2 | νCH | B_2 | B_{2g} | IR, R | R |

* Falls with increasing temperature

** Band with complex structure and qualitative changes with increasing temperature ($L = B_{2g}$)

state. On increasing the temperature the percentage of the planar form increases at the expense of the nonplanar forms [105].

d. **Compounds with cyclobutane rings.** As in the case of other cycloalkanes the most useful vibrations for diagnostic purposes are those of the methylene group.

$\nu\text{C}-\text{C}$ ring vibrations are less characteristic. They give rise to low intensity bands and very often are inactive in the infrared.

1. *C—H stretching modes.* In cyclobutane the *stretching modes* of methylene groups are shifted towards higher values: 2896 cm^{-1} (νCH_2 , sym) and 2974 cm^{-1} (νCH_2 , asym) [100, 65]. The shift is due to the abnormal character of bonds in this hydrocarbon, which is a transition between the strained three-membered ring and nonstrained rings [84, 107].

In cyclobutanes substituted with various functional groups (halogen, carbonyl, nitrile etc.), C—H frequencies fall in this range [50]. Three bands arise in the $2900\text{--}2985\text{ cm}^{-1}$ region at narrow intervals: $2980\text{--}2985\text{ cm}^{-1}$, $2938\text{--}2954\text{ cm}^{-1}$, and $2922\text{--}2925\text{ cm}^{-1}$. They are considered characteristic for this system. The majority of substituted cyclobutanes show an additional band at $2855\text{--}2871\text{ cm}^{-1}$. In methyl- and ethylcyclobutane this band was assigned to the CH_3 or C_2H_5 group; however, it cannot be explained in the same way in amino or halogen compounds [50].

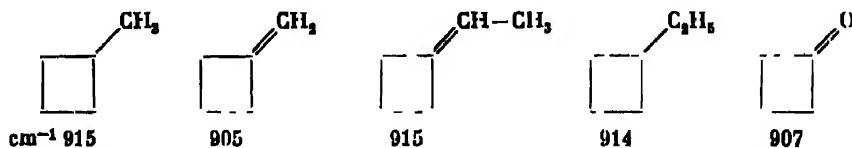
2. *CH deformation modes.* The scissoring mode of CH_2 groups in cyclobutane has a lower frequency (1444 cm^{-1}) [100] as compared to nonstrained rings [58].

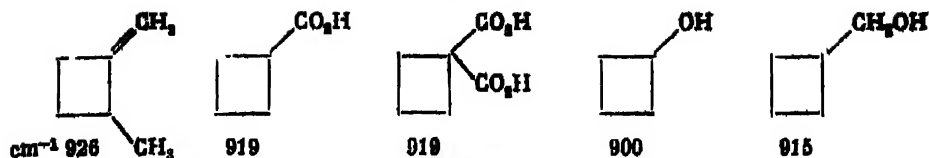
The in-plane rocking mode of the CH_2 group (γCH_2), characteristic for saturated hydrocarbons, is the most studied one in the cyclobutane series. In cyclobutane itself this vibration was assigned the 901 cm^{-1} band. Its position is different from that of the corresponding absorption in cyclopropane (741 cm^{-1}) or in normal alkanes (720 cm^{-1}). It is inactive in Raman and gives rise to a medium intensity absorption in the infrared [65, 99, 100].

For the characterization of substituted cyclobutane rings several bands between 800 and 1000 cm^{-1} were proposed with special emphasis on three regions: $868\text{--}888\text{ cm}^{-1}$ [106], $900\text{--}923\text{ cm}^{-1}$ [97], and $960\text{--}1000\text{ cm}^{-1}$ [60]. For bands arising at $838\text{--}888\text{ cm}^{-1}$ and $960\text{--}1000\text{ cm}^{-1}$ no definite assignments were made. The band arising at $900\text{--}923\text{ cm}^{-1}$ in spectra of monoalkylcyclobutanes was assigned to the CH_2 rocking modes of the cyclobutane ring [97]; however, since it is not observed in all four-membered ring compounds, it is of little value for diagnostic purposes [65].

In a number of substituted derivatives of cyclobutane (with NH_2 , COOH , CN , halogen groups, etc.), bands in the $907\text{--}957\text{ cm}^{-1}$ range were assigned to characteristic vibrations of the cyclobutane ring [61].

A more complete critical study based on literature data and on the analysis of a great number of cyclobutanes substituted with various functional groups has shown that all compounds in which the four-membered ring has at least one unsubstituted CH_2 group absorb in the $900\text{--}950\text{ cm}^{-1}$ range. The band arises in all physical states of the respective compound and is assigned to the in-plane rocking vibration γCH_2 [65]. Frequencies observed in some representative compounds are shown below:





The converse of this rule is not valid, since a great many organic molecules not containing cyclobutane rings give rise to absorptions in this region as well.

3. *Ring vibrations.* One of the characteristic vibrations of various rings is the so-called "ring-breathing" vibration: the carbon atoms first shift apart and then come closer together in a motion equally involving the whole ring. In cyclobutane compounds this vibration mode gives rise to frequencies in the range 950–1000 cm^{-1} . The band is strong in Raman spectra (970 cm^{-1}); in the infrared it is active only in molecules without a symmetry center.

In conclusion, it can be stated (as in the case of three-, five-, and six-membered rings) that no frequency arising from the four-membered ring can be used as the only criterion for the identification of this ring. A band present in the range 900–950 cm^{-1} can confirm a cyclobutane structure only if it is implemented by data arising from other regions of the spectrum and/or by other methods of investigation [65].

c. Bridged bicyclic and polycyclic compounds

In strain-free systems frequencies of C—H and C—C stretching and deformation modes arise within normal ranges for the corresponding cycloalkane.

In strained systems some particular aspects are observed. As in the case of small rings, relief of strain imposed by the geometry of the molecule results in rehybridization of carbon atoms. Consequently, vibrations of bands enriched in *s*-component will arise at higher frequencies, while vibrations of bands enriched in *p*-component will arise at lower frequencies than normal. The change in hybridization is not the same for all atoms of a strained system. It could be shown that it is localized on the atoms most involved the strain.

In the infrared the most important vibrations can be observed in stretching and deformation modes of CH_2 and tertiary CH groups.

a. *Stretching modes of the CH_2 group.* The frequency of νCH_2 vibrations increases as the ring size decreases; for example, in five-membered rings, the frequency is 10–40 cm^{-1} higher than in six-membered rings. In strained compounds the bands corresponding to the CH_2 group arise at 2922 and 2982 cm^{-1} , while in relatively nonstrained compounds they arise at 2878 and 2950 cm^{-1} [107]. The difference ($\Delta\nu$, in cm^{-1}) between the symmetrical and asymmetrical CH_2 stretching modes is, as in the case of *n*-alkanes, relatively constant (60–90 cm^{-1}). This is of value for the assignment of νCH_2 bands in the 2800–3000 cm^{-1} region. Furthermore, it shows that methyl groups can be characterized by the mean value (νCH_2m) of symmetrical and asymmetrical vibration frequencies:

$$\nu\text{CH}_2m = (\nu\text{CH}_2\text{ asym} - \nu\text{CH}_2\text{ sym})/2.$$

Taking for reference the νCH_2 frequency 3035 cm^{-1} in halo-(Cl, Br)-cyclopropane (in which the $\text{C}-\hat{\text{C}}-\text{C}$ angle is considered to be 60°) [108] and the νCH_2 frequency 2890 cm^{-1} in a chain of a normal alkane ($\text{C}-\hat{\text{C}}-\text{C} = 109^\circ$), a linear relationship between the mean value of the methylene group frequency and the valence angle could be established. This relationship was used to determine $\text{C}-\hat{\text{C}}-\text{C}$ angles in a number of mono- and polycyclic systems [109].

A number of analyzed systems are shown below. The corresponding observed frequencies are shown in Table II-16.

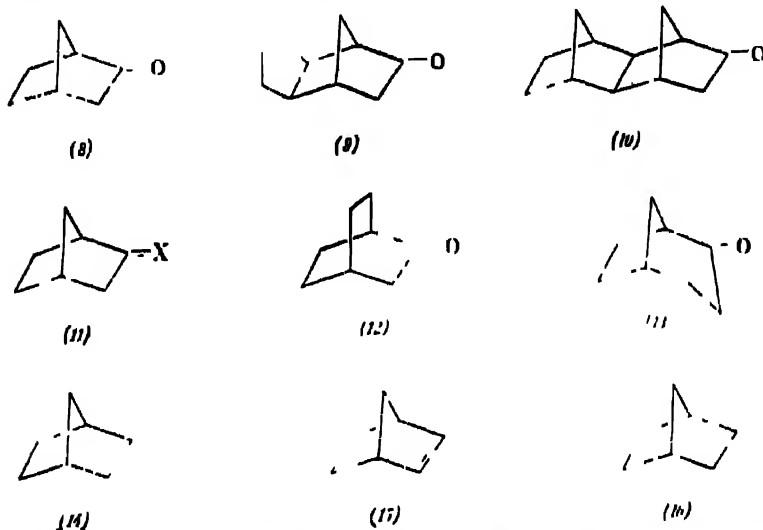


Table II-16 Characteristic frequencies $\nu\text{CH}(\text{cm}^{-1})$ in bridged bi- and polycyclic system [100]

| Compound | No. of atoms in ring | νCH_2 , asym | νCH_2 , sym | νCH_2 , asym- νCH_2 , sym | νCH_2 , m | No. of ring CH_2 groups | νCH (bridge-head) | νCO |
|----------|----------------------|-------------------------|------------------------|--|----------------------|----------------------------------|------------------------------|----------------|
| (8) | 5 | 2969 | 2883 | 86 | 2926 | 5 | 2918 | 1751 |
| (9) | 5 | 2958 | 2868 | 90 | 2913 | 5 | 2929 | 1750 |
| (10) | 5 | 2956 | 2887 | 69 | 2922 | 5 | — | 1748 |
| (11) | 5 | 2951 | 2877 | 74 | 2914 | 5 | — | 1768 |
| (12) | 6 | 2948 | 2873 | 75 | 2910 | 6 | 2915 | 1731 |
| (13) | 6 | 2944 | 2870 | 74 | 2907 | 6 | — | 1717 |
| (14) | 5 | 2955 | 2871 | 84 | 2913 | 6 | 2920 | — |
| (15) | 5 | 2940 | 2871 | 69 | 2905 | — | 2987 | — |
| (16) | 5 | 2974 | — | — | — | — | 2924 | — |
| | | | | | | | 2907 | — |

It has been shown that the angle between carbon atoms forming the methylene bridges can vary within large limits as a function of the structure of the molecule. In compounds (8--14) this angle has approximately the same value (100°). An increase in the bridge CH_2 group bond angle is observed in going from bicyclo [2.2.1] heptane (101°) to bicyclo [2.2.1] heptadiene-2,5 (104°). The different character of positions 1 and 4 can be observed in Fig. II-30

since angles α of the double bonds are more rigid and their deviation from 120° is more difficult to achieve, the strain arising in the system is compensated by the decrease of angle β at positions 1 and 4 and the increase of angle $C-\hat{C}-C$ at position 7. This phenomenon results in an almost normal frequency of the bridge CH_2 group in (15) and a much higher frequency of the bridgehead $C-H$ bond (positions 1 and 4), as compared to (8, 12, 14 and 16) (see vibration of tertiary $C-H$, this Chapter, Section 3,c,b).

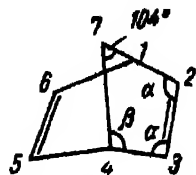


Fig. 11-30 Bicyclo [2.2.1] heptadiene 2,5

In stereoisomeric *syn*- and *anti*-tricyclo [4.2.0.0^{2,5}] octanes the CH_2 groups of the outside cyclobutane rings give rise to frequencies at 2852 and 2952 cm^{-1} and 2852 and 2938 cm^{-1} in the *anti* (17) and *syn* (18) configurations, respectively. The spectra of these compounds are shown in Fig 11-31 [110].

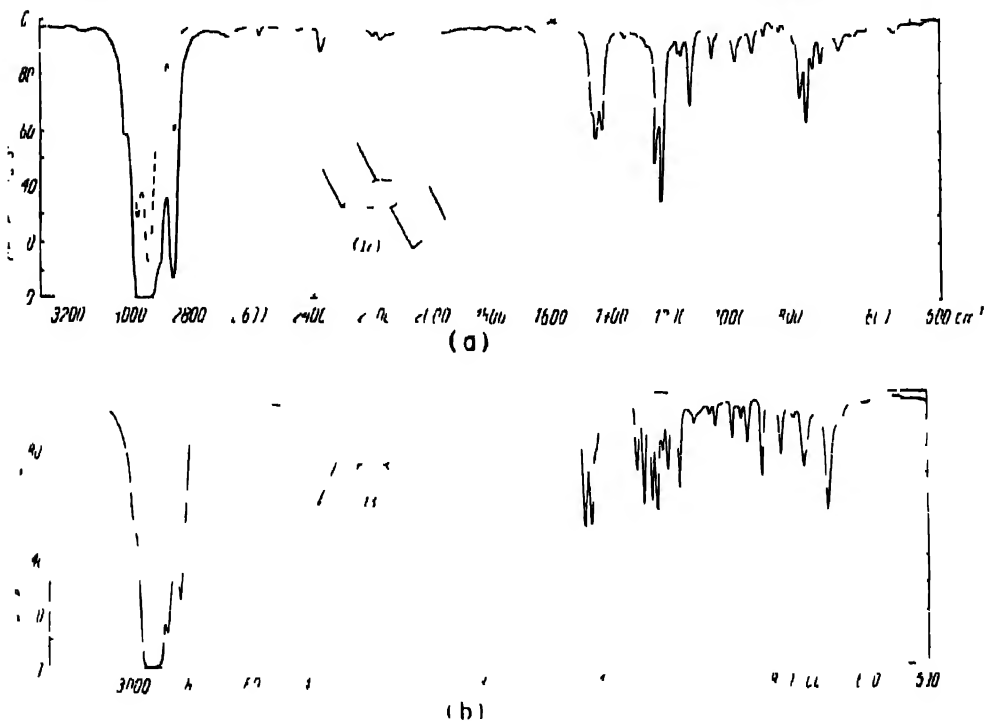


Fig. 11-31 Infrared spectrum of tricyclo [4.2.0.0^{2,5}] octane (a) *anti*-form; (b) *syn*-form

The spectrum of bicyclo [2.2.0] hexane (19) shows two strong bands at 2890 and 2835 cm^{-1} [111]. Bicyclo [2.1.0] pentane (20) gives rise to absorptions at 2871 and 2955 cm^{-1} [112].

Nortricyclene (21) absorbs at 3070 cm^{-1} [113] and adamantane (22) at 2857 and 2933 cm^{-1} [114].

In a number of bridged polycyclic compounds (23–30) containing sterically opposite and sufficiently close CH_2 groups, an increase in frequency of the C-H bands was observed [115–117].

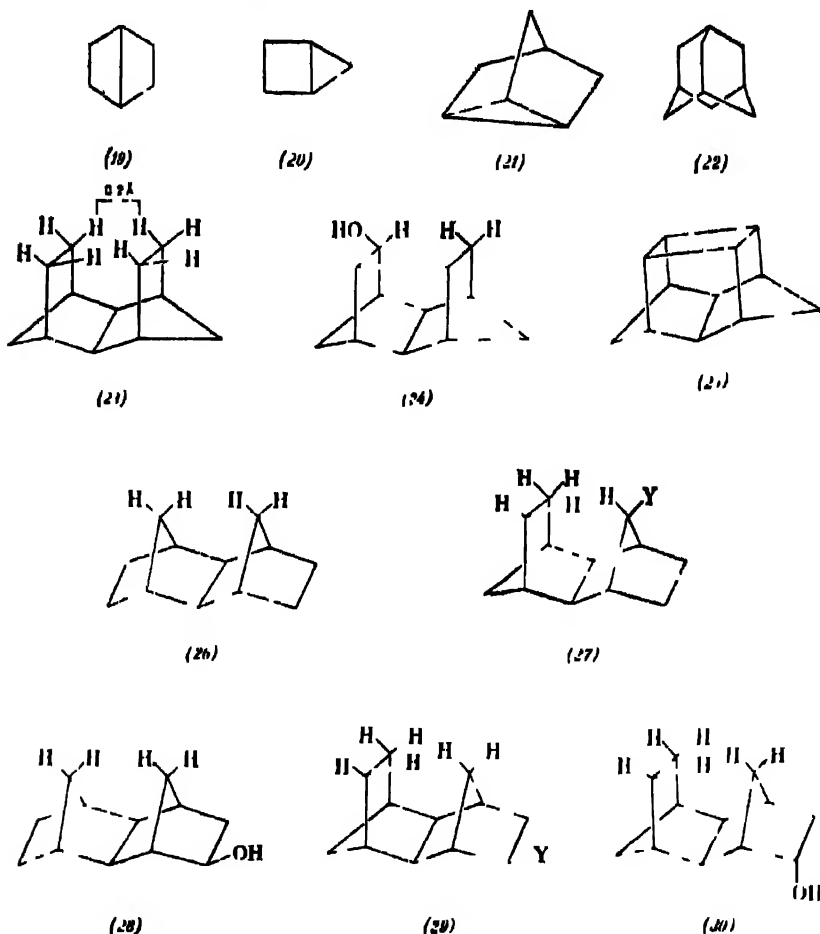


Table II-17 $\nu(\text{H})$ frequency (cm^{-1}) in bridged polycyclic compounds [116]

| Compound | 1 | 2 | 3 | 4 |
|----------------|------|------|------|------|
| (23) | 3031 | 2952 | — | 2885 |
| (24) | 3049 | 2983 | — | 2891 |
| (25) | — | 2967 | — | 2871 |
| (26) | 3052 | 2959 | 2930 | 2881 |
| (27) | 3037 | 2954 | 2918 | 2894 |
| (28) | 3040 | 2955 | 2921 | 2879 |
| (29) | 3049 | 2955 | 2911 | 2887 |
| Cyclodecanol | 2991 | 2930 | 2868 | 2849 |
| Cyclododecanol | — | 2941 | 2868 | 2857 |

The distance between neighboring hydrogen atoms are 0.2\AA in (23), 0.9\AA in (24), 1.1\AA in (26), and 1.3\AA in (27). The steric configuration is *endo-endo* in compound (23), *exo-exo* in (26), and *endo-exo* in (27). Compound (24) has a *half-cage* structure and (25) forms a *cage*.

The corresponding frequencies are shown in Table II-17.

The frequencies of cyclodecanol (sterically compressed) and of cyclo-dodecanol (CH bonds sterically free) were introduced in this table for reference. The νCH_2 asym vibrations (Column 2) and νCH_2 sym vibrations (Column 4) give rise to frequencies about 30 cm^{-1} higher than normal. Values in Column 3 correspond to stretching vibrations of tertiary >CH groups. In compounds (24) and (25) the band at 2960 cm^{-1} is particularly strong which leads to the assumption that the tertiary CH band overlaps with the CH_2 band. Frequencies in Column 1 correspond to weak bands assigned to asymmetrical stretching vibrations of the sterically opposite CH_2 groups. The frequencies of the symmetrical vibrations of these groups are probably shifted by $30\text{--}100\text{ cm}^{-1}$ with respect to values in Column 4. The frequency difference in Columns 1 and 2 measures the extent of reciprocal perturbation of vibrations arising from the two sterically close CH_2 groups. The

Table II-18 Frequency and intensities of sterically opposed νCH_2 bands [117]

| Compound | Frequency cm^{-1} | $A \cdot 10^3 \text{ cm}^2/\text{molecule} \cdot \text{sec}$ | $A/\text{CII}_2 (10^3 \text{ cm}^2/\text{group} \cdot \text{sec})$ |
|----------|-------------------------------|--|--|
| (28) | 3049 | 20.2 | 10.1 |
| (29) | 3051 | 11.7 | 3.9 |
| (30) | 3052 | 13.7 | 4.6 |
| (24) | 3043 | 14.8 | 5.9 |

variation of the integrated intensity A of bands arising from sterically opposite CH_2 groups in compounds (28–30) and (24) is shown in Table II-18. In this table the intensities are referred both to the whole molecule and to individual sterically opposed CII_2 units.

b. **Stretching mode of the tertiary CH bond (*tert* $\nu\text{C-H}$).** In alkanes the *tert* $\nu\text{C-H}$ vibration gives rise to a weak absorption at about 2890 cm^{-1} . In bridged polycyclic systems the frequency corresponding to this vibration increases by $20\text{--}100\text{ cm}^{-1}$ as compared to *n*-alkanes or triphenylmethane [118]. The phenomenon was explained by the increase in *s*-character of the >C-H bond as a result of changes in the sp^3 hybridization of the bridge-head carbon; this change relieves to some extent the strain introduced by bridging. Investigation of the region corresponding to C-H vibrations in a number of bridged bi- and polycyclic systems (Tables II-16 and II-19) has

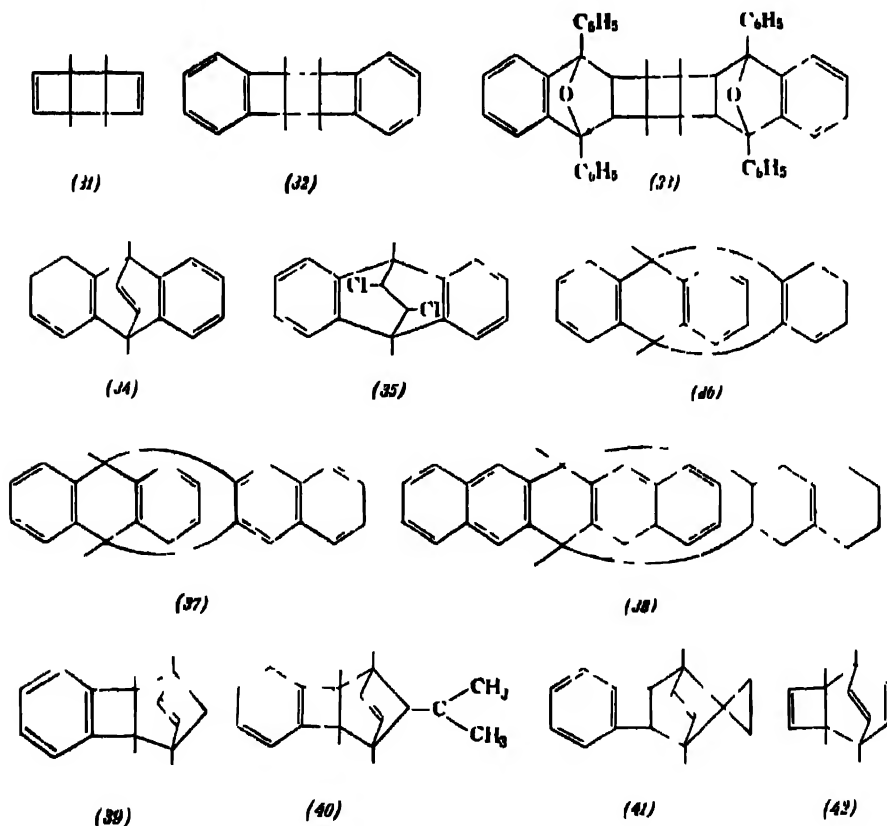
Table II-19 CH Frequencies and force constants of some polycyclic compounds [118]

| Compound | Recorded in | νCH cm^{-1} | $k \cdot 10^{-4}$ dyn/cm | Compound | Recorded in | νCH cm^{-1} | $k \cdot 10^{-4}$ dyn/cm |
|----------|----------------|------------------------------------|--------------------------------------|----------|----------------|------------------------------------|--------------------------------------|
| (31) | CCl_4 | 2987 | 4.737 | (37) | KBr | 2965 | 4.730 |
| | | 2975 | 4.762 | (38) | KBr | 2965 | 4.730 |
| (32) | CCl_4 | 2968 | 4.740 | (39) | CCl_4 | 2962 | 4.721 |
| (33) | CCl_4 | 2960 | 4.712 | (40) | CCl_4 | 2958 | 4.708 |
| (34) | KBr | 2979 | 4.776 | (41) | CCl_4 | 2958 | 4.708 |
| (35) | KBr | 2980 | 4.778 | (42) | CCl_4 | 2920 | 4.588 |
| (36) | KBr | 2984 | 4.727 | | | 2962 | 4.721 |

shown that in bridged saturated bicyclic systems the shift is approximately 30 cm^{-1} (compounds 8, 9, and 14) (Table II-16); this shows that the distortion of valence angles of the bridgehead carbon atoms is negligible. In bicyclo [2.2.1] heptadiene 2,5 (15) the double bonds require that the angle between atoms 2,3 and 5,6 be maintained at ca 120° (Fig. II-30) which leads to the decrease of the angles at atoms 1 and 4; the *tert* $\nu\text{C}-\text{H}$ frequency rises to 2987 cm^{-1} .

The very small shifts in frequency in the bicyclo [2.2.2] -octane system indicate an almost complete absence of strain; this can be seen in the model shown in Fig. II-32 [118].

The unsaturation in the bridge results in a change of the steric configuration of the molecule; the strain is concentrated mainly at the level of the bridgehead carbons. In 9,10-dihydro-9,10-ethanoanthracene (34) the νCH frequency is 2979 cm^{-1} . Values of the same order of magnitude are also found in triptycene compounds (36–38).



In triene (42) with a tricyclo [1.2.2.0^{2,5}] decane skeleton, absorptions arising from the two types of *tert* CH bonds could be assigned on the basis of the geometrical model of the molecule. In this model the orientation of

valencies of the unsaturated (sp^2 hybridized) carbons was assumed to be rigid, while that of saturated carbon atoms was assumed to be nonrigid. As can be seen in Fig. II-33, in compound (42) maximum strain arises at carbon atoms 2 and 5. Consequently, the 2962 cm^{-1} band was assigned to the CH

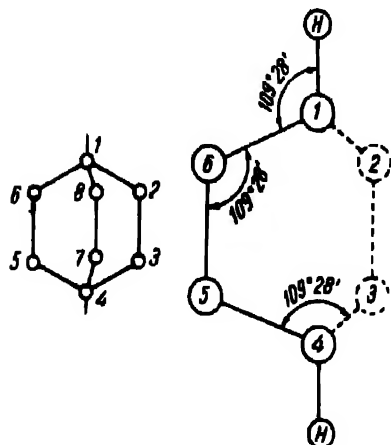


Fig. II-32 Bicyclo [2.2.2] octane skeleton

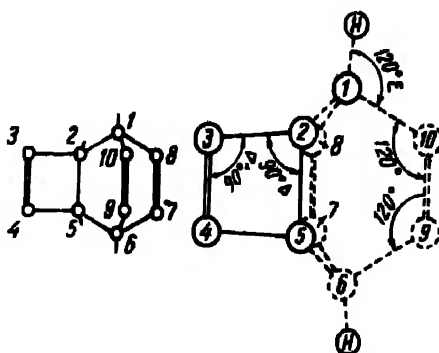


Fig. II-33 Tricyclo [4.2.0.0^{2,5}] decatriene skeleton.

bonds 2 and 5, and the 2920 cm^{-1} band was assigned to the less strained bridgehead bonds (1,6). The infrared spectrum of compound (42) is shown in Fig. II-36.

In molecules having the tricyclo [4.2.0.0^{2,5}] octane skeleton the *tert* CH frequency in four-membered rings is shifted by ca. 77 cm^{-1} . Although larger strain (and shifts) are to be expected for these systems, the smaller experimental values are probably due to the abnormal character of bonds in the cyclobutane ring (see Table II-19, compounds 31, 32 and 42 and Fig. II-34).

In the symmetrical strain free adamantane molecule (22), the *tert* CH frequency arises at 2907 cm^{-1} .

The force constants of bridgehead *tert* C—H bonds (calculated from the observed frequencies show that these bonds are intermediate between simple C—H bonds of saturated carbon atoms with sp^3 hybridization ($\kappa \approx 1.5 \cdot 10^5\text{ dyn. cm}^{-1}$) and C—H bonds of unsaturated carbon atoms with sp^2 hybridization ($\kappa \approx 5.0 \cdot 10^5\text{ dyn cm}^{-1}$) (Table II-19).

The strained symmetrical molecule of cubane (42a) has a spectrum with few bands. The stretching modes of the four *tert* C—H bonds give rise to a strong absorption at 3000 cm^{-1} . The spectrum shows two more bands at 1231 and 851 cm^{-1} [115].

c. **Deformation modes.** Deformation modes of strained bonds have frequencies lower than normal. In bicyclo [2.2.0] hexane (19) the band arising from the deformation mode appears at 1433 cm^{-1} [111] and in tricyclo [4.2.0.0^{2,5}] octadiene-3,7 it appears at 1298



(42a)

cm^{-1} [110, 119]. In cubane the frequency of the deformation mode falls to 1231 cm^{-1} [115]. *anti*-Tricyclo [4.2.0.0^{1,5}] octane absorbs at 1438 and 1460 cm^{-1} with a shoulder at 1470 cm^{-1} ; *syn*-tricyclo [4.2.0.0^{2,5}] octane absorbs at 1438 and 1460 cm^{-1} with a shoulder at 1462 cm^{-1} (see Fig. II-31b).

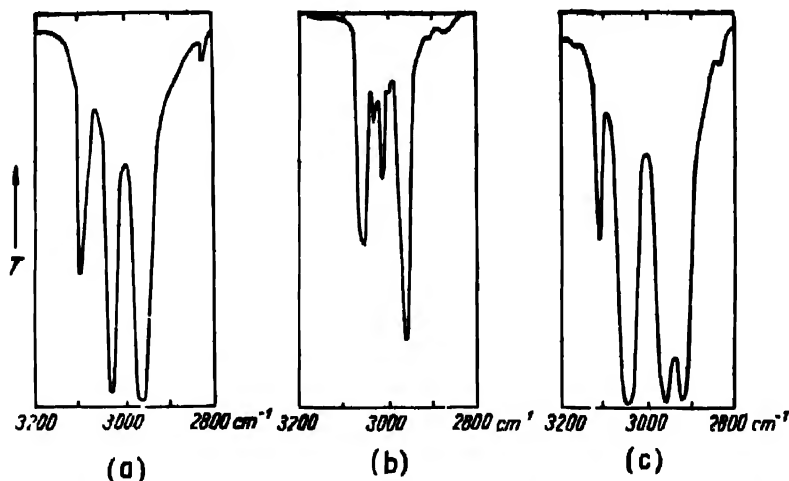


Fig. II-34 Region of the CH stretching mode in infrared spectra of some tricyclic compounds:

(a) tricyclo [4.2.0.0^{1,5}] octadiene-3, 7 [119]; (b) 3,4,7,8-dibenzotricyclo [4.2.0.0^{1,5}] octadiene-3, 7 [118]; (c) tricyclo [4.2.2.0^{1,5}] decatriene-3,7,9 [118].

B. UNSATURATED HYDROCARBONS

1. Acyclic alkenes

The interpretation of infrared spectra of alkenes is based on the complete vibrational analysis of ethylene and deuterated ethylene, as well as on empirical studies of spectra of a great many compounds with one or several C=C double bonds.

a. Ethylene

Vibrational spectra of ethylene and deuterioethylene have been extensively studied [120, 121] and assignments of fundamental vibration modes of this molecule have been made. For theoretical reasons the ethylene molecule is considered to be planar and belongs to the symmetry class V_h (Fig. II-35) [120]. The validity of the mutual exclusion rule (see page 97) in Raman and infrared spectra supports the centrosymmetric structure of ethylene in the gaseous state. The twelve normal vibration modes of ethylene C_2H_4 and deuterioethylene C_2D_4 are

$$3A_g(\text{R}), A_u(\text{IR}), 2B_{1g}(\text{R}), B_{1u}(\text{IR}), B_{2g}(\text{R}), 2B_{2u}(\text{IR}).$$

The assignments of fundamental frequencies [120, 121] are shown in Table II-20.

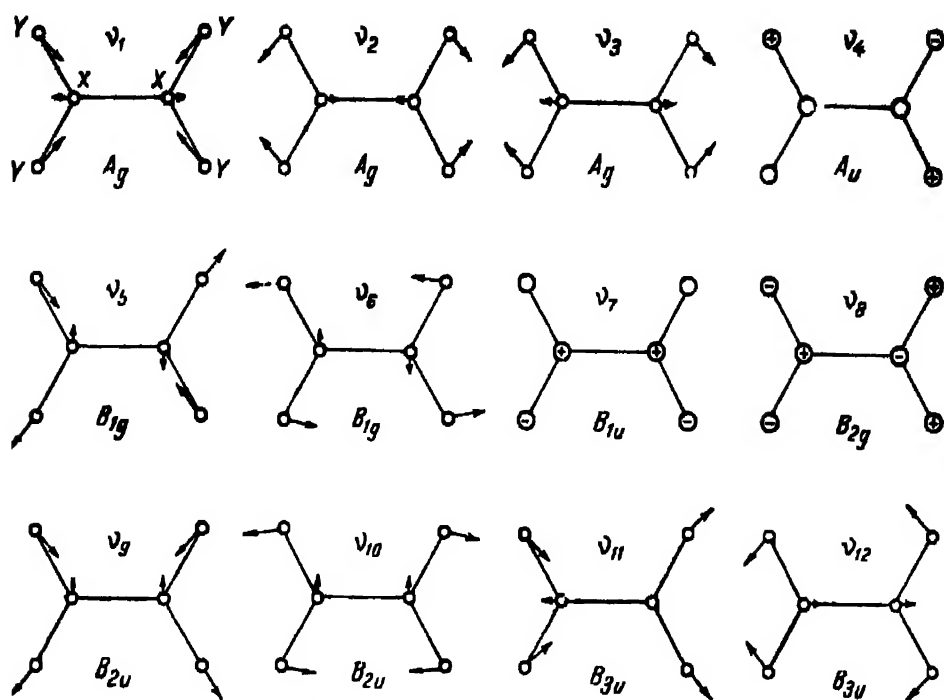


Fig. 11-35 Normal vibration modes of ethylene (point group V_h).

Table II-20 Fundamental frequencies in spectra of C_2H_4 and C_2D_4 , cm^{-1} [120]

| Assign- ment | Species | C_2H_4 | | C_2D_4 | | Type of vibration |
|-----------------|----------|-------------|----------------|-------------|-----------------|----------------------------|
| | | IR (gas) | Raman (gas) | IR (gas) | Raman liquid | |
| ν_4 | A_u | (825) | — | (580) | — | δCH_2 l |
| ν_5 | B_{1g} | — | 94.3 | — | 780 | δCH_2 out-of-plane |
| ν_7 | B_{1u} | 942.2 | — | 720.0 | — | δCH_2 out-of-plane |
| ν_{10} | B_{2u} | 985 | — | (712) | — | γCH_2 r |
| ν_6 | B_{1g} | — | (1050) | — | (883) | γCH_2 r |
| ν_8 | A_g | — | 1343.4 | — | 981 | δCH_2 in-plane |
| ν_{10} | B_{2u} | 1443.5 | — | 1077.5 | — | δCH_2 in-plane |
| ν_9 | A_g | — | 1623.3 | — | 1515 | $\nu C=C$ |
| ν_{11} | B_{2u} | 2989.5 | — | 2200.2 | — | νCH sym |
| ν_1 | A_g | — | 3019.3 | — | 2251 | νCH asym |
| ν_6 | B_{2u} | 3105.5 | — | 2345 | — | νCH asym |
| ν_2 | B_{1g} | — | 3272.3 | — | 2304 | νCH asym |

Note. In other interpretations [121] to the vibrations ν_4 , ν_{10} , ν_6 , and ν_2 have been assigned the frequencies of 1027, 810, 1236, and 3075 cm^{-1} .

b. Substituted ethylenes

The main types of vibrations giving rise to characteristic bands in infrared spectra of alkenes are stretching vibrations $\nu\text{C}=\text{C}$ (generally speaking, one band for each double bond) and stretching and deformation vibrations of hydrogen atoms directly linked to the carbon atom of the double bond. These vibrations take place in plane and out of plane of the molecule (one each for every hydrogen atom present [120]).

The following spectral regions are important for diagnostic purposes:

1. $\text{C}=\text{C}$ stretching vibration ($1580\text{--}1680\text{ cm}^{-1}$);
2. $\text{C}-\text{H}$ stretching vibration ($3000\text{--}3100\text{ cm}^{-1}$);
3. out-of-plane $\text{C}-\text{H}$ deformation vibration ($680\text{--}1000\text{ cm}^{-1}$);
4. deformation vibration of the CH_2 group adjacent to the double bond (about 1430 cm^{-1}).

a. $\text{C}=\text{C}$ stretching vibrations. In theory, the vibration of an isolated $\text{C}=\text{C}$ double bond should be active only in Raman spectra. The band is very strong because of the high polarizability of the double bond. The inactivity of this band in the infrared is due to molecular symmetry.

However, because of the perturbation of the electronic system of the double bond produced by substituents, the $\text{C}=\text{C}$ stretching vibration can give rise to weak absorptions in the IR. If the substituents at the double bond are identical or distributed in such a way that the molecule maintains its center of symmetry, the band becomes too weak to be identified.

Generally speaking, in simple alkenes the $\nu\text{C}=\text{C}$ frequency occurs within the range $1640\text{--}1680\text{ cm}^{-1}$ [122, 123]. The position and intensity of the absorption band depend on the nature, mode, and extent of substitution of the $\text{C}=\text{C}$ double bond. Mean values for different types of alkenes are shown in Table II-21.

The $\nu\text{C}=\text{C}$ frequency in alkenes monosubstituted with alkyl groups arises at the lower limit of the range. The corresponding bands occur at 1643 cm^{-1} and are of medium intensity (see Table II-22). An increasing number of alkyl groups shifts the absorption bands towards higher frequencies. Asymmetrically disubstituted ethylenes absorb in the range $1640\text{--}1660\text{ cm}^{-1}$ (see Table II-23). *cis*-Isomers of symmetrically disubstituted ethylenes show a $\nu\text{C}=\text{C}$ absorption band at 1657 cm^{-1} . In the more symmetrical *trans* isomers the frequency is higher, but the decrease in intensity (see above) makes its detection difficult in most cases.

In ethylenes substituted with higher alkyls, $\text{R}_1\text{CH}=\text{CHR}_2$ the frequency is only slightly lower ($\sim 5\text{ cm}^{-1}$) (see Table II-24). However, a *tert* butyl group decreases the $\nu\text{C}=\text{C}$ frequency substantially. In sym di-*tert* butylethylene $(\text{CH}_3)_3\text{CH}-\text{C}=\text{C}-\text{CH}(\text{CH}_3)_3$, the band occurs at 1631 cm^{-1} . The effect of the *t*-butyl group can be seen in 2,3,3-trimethylbutene-1, $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$, which absorbs at 1639 cm^{-1} (see Table II-23). It is thought that this shift is due to some extent to steric factors [121]. $\nu\text{C}=\text{C}$ frequencies of some di-, tri-, and tetrasubstituted alkenes are shown in Tables II-24 and II-25.

Table II-21 Mean frequencies $\nu_{C=C}$ in various types of alkenes

| Alkene | Formula* | $\nu_{C=C}$, cm^{-1} |
|------------------------------------|--|--------------------------------|
| Monosubstituted | $\text{RCH}=\text{CH}_2$ | 1643 |
| asym disubstituted | $\begin{array}{c} \text{R}_1 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R} \end{array} \quad \text{CH}_2$ | 1653 |
| sym disubstituted (<i>trans</i>) | $\begin{array}{c} \text{R}_1 \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{R}_2 \end{array}$ | 1673 |
| sym disubstituted (<i>cis</i>) | $\begin{array}{c} \text{R}_1 \quad \quad \text{R}_2 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \end{array}$ | 1657 |
| trisubstituted | $\begin{array}{c} \text{R}_1 \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \quad \text{R}_2 \end{array}$ | 1674 |
| tetrasubstituted | $\begin{array}{c} \text{R}_1 \quad \quad \text{R}_2 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{R}_3 \quad \quad \text{R}_4 \end{array}$ | — |

* R — alkyl

Table II-22 $\nu_{C=C}$ frequency in mono-substituted ethylenes $\text{RCH}=\text{CH}_2$ [121]

| Alkene | R | Frequency, cm^{-1} |
|----------------------|---------------------------------------|-----------------------------|
| Propene | CH_3 | 1647 |
| Butene-1 | CH_3CH_2 | 1645 |
| Pentene-1 | $(\text{CH}_2\text{CH}_2)_2\text{CH}$ | 1647 |
| Hexene-1 | $\text{CH}_3(\text{CH}_2)_3$ | 1642 |
| 3-Methylbutene-1 | $(\text{CH}_3)_2\text{CH}$ | 1644 |
| 3,3-Dimethylbutene-1 | $(\text{CH}_3)_3\text{C}$ | 1645 |

Table II-23 $\nu_{C=C}$ frequency in asymmetrically disubstituted ethylenes [121]

| Alkene | R_1 | R_2 | Frequency cm^{-1} |
|-------------------------|------------------------|----------------------------|----------------------------|
| Isobutene | CH_3 | CH_3 | 1661 |
| 2-Methylbutene-1 | CH_3 | C_2H_5 | 1652 |
| 2-Methylpentene-1 | CH_3 | $n\text{C}_4\text{H}_9$ | 1653 |
| 2-Methylheptene-1 | CH_3 | $n\text{C}_6\text{H}_{13}$ | 1656 |
| 2-Ethylbutene-1 | C_2H_5 | C_2H_5 | 1647 |
| 2,3,3-Trimethylbutene-1 | CH_3 | $(\text{CH}_3)_2\text{C}$ | 1639 |

As shown, the intensity of the $\nu_{C=C}$ band is generally weak and decreases as the symmetry of the molecule increases. The highest intensity is observed in alkenes with a terminal, vinyl double bond. The more the double bond

Table II-24 $\nu_{C=C}$ frequency in symmetrically disubstituted ethylenes $R_1CH=CHR_2$ [121]

| Alkene | R_1 | R_2 | Frequency, cm^{-1} | |
|--------------------------------|-------------|-------------|----------------------|--------------|
| | | | <i>cis</i> | <i>trans</i> |
| Butene-2 | CH_3 | CH_3 | 1661 | — |
| Pentene-2 | CH_3 | C_2H_5 | 1658 | — |
| Hexene-2 | CH_3 | $n-C_3H_7$ | 1657 | (1670) |
| Hexene-3 | C_2H_5 | C_2H_5 | 1656 | — |
| Heptene-3 | C_2H_5 | $n-C_3H_7$ | 1656 | — |
| Octene-4 | $n-C_3H_7$ | $n-C_3H_7$ | 1650 | (1670) |
| 2, 2, 5, 5 Tetramethylhexene 3 | $(CH_3)_3C$ | $(CH_3)_3C$ | 1631 | — |

Table II-25 $\nu_{C=C}$ frequency in tri- and tetrasubstituted ethylenes [121]

| Alkene | Formula | Frequency, cm^{-1} |
|---------------------------------|--|----------------------|
| 2-Methylbutene-2 | $\begin{array}{c} CH_3 \\ \diagdown \\ C - C - CH_3 \\ \diagup \\ CH_3 \end{array}$ | 1681 |
| 2-Methylpentene-2 | $\begin{array}{c} CH_3 \\ \diagdown \\ C - CHCH_3 - CH_3 \\ \diagup \\ CH_3 \end{array}$ | 1675 |
| <i>cis</i> -3-Methylpentene-2 | $\begin{array}{c} CH_3 \quad \quad CH_3 \\ \diagdown \quad \diagup \\ C - C \\ \diagup \quad \diagdown \\ H \quad \quad CH_2 \quad CH_3 \\ CH_3 \quad \quad CH_2 \quad CH_3 \end{array}$ | 1675 |
| <i>trans</i> -3-Methylpentene-2 | $\begin{array}{c} CH_3 \quad \quad CH_3 \\ \diagdown \quad \diagup \\ C - C \\ \diagup \quad \diagdown \\ H \quad \quad CH_2 \quad CH_3 \\ CH_3 \quad \quad CH_2 \quad CH_3 \end{array}$ | |
| 2, 2, 4-Trimethylpentene-3 | $(CH_3)_3C - CH - C(CH_3)_2$ | 1664 |

is shifted towards the center of the chain, the lower the intensity of the band. In symmetrically disubstituted alkenes, the extinction coefficient of the *cis* isomers is ca. five times higher than that of the *trans* isomer.

b. **$=C-H$ stretching vibrations.** Stretching vibrations of hydrogen atoms directly attached to the double bond give rise to the most characteristic absorptions in infrared spectra of alkenes. The bands lie in the range $3000-3100\text{ cm}^{-1}$. The increase of the $C-H$ vibration frequency in alkenes, cf. saturated hydrocarbons, is due to the sp^2 hybridization of the carbon atom which increases the amount of s component in the $C-H$ bond. The force constant of these bonds is larger than that of $C-H$ bonds in alkenes (where carbon atoms have sp^3 hybridization).

Ethylene has four stretching vibrations in the range $2990-3166\text{ cm}^{-1}$ (see Table II-20).

On substitution of hydrogen atoms in ethylene with alkyl groups, the low frequency vibration is often shielded by the vibrations of $C-H$ bonds

arising from the saturated portion of the molecule. For this reason alkenes are generally characterized by absorptions above 3000 cm^{-1} .

The position of the absorption band arising from this vibration depends on the mode of substitution of the $\text{C}=\text{C}$ double bond.

The position and number of bands in this region enables the differentiation between various types of alkenes (see Table II-26). Alkenes with terminal double bonds (vinyl compounds) have the highest frequencies. Asymmetrically mono- and disubstituted ethylenes show a band in the range $3075\text{--}3090\text{ cm}^{-1}$ with an extinction coefficient of 25–35. Compared with asymmetrically disubstituted ethylenes, monosubstituted ethylenes have an additional band in this region at $3012\text{--}3025\text{ cm}^{-1}$. This band was assigned to the vibration of the hydrogen atom in 2-position ($-\overset{2}{\text{CH}}=\overset{1}{\text{CH}}_2$),

Table II-26 νCH frequencies in alkenes

| Alkene | Formula | Frequency, cm^{-1} |
|----------------------|---|--------------------------------|
| Propene | $\text{CH}_3\text{CH}=\text{CH}_2$ | 3081, 3012 |
| Butene 1 | $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ | 3086 |
| Pentene 1 | $\text{CH}_3(\text{CH}_2)_2\text{CH}=\text{CH}_2$ | 3075 |
| Isobutene | $(\text{CH}_3)_2\text{C}=\text{CH}_2$ | 3086 |
| 3,3-Dimethylbutene 1 | $(\text{CH}_3)_3\text{C}-\text{CH}=\text{CH}_2$ | 3095 |
| cis-Butene 2 | $\text{CH}_3\text{CH}=\text{CHCH}_3$ | 3030 |
| trans-Butene 2 | | 3021 |
| cis-Pentene-2 | $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$ | 3018 |
| trans-Pentene 2 | | 3027 |

while the higher frequency band is assigned to vibrations of the two terminal hydrogens of the $=\text{CH}_2$ group. Symmetrically disubstituted ethylenes, with an internal double bond, $\text{RCH}=\text{CHR}$, have a single low frequency band at $3012\text{--}3025\text{ cm}^{-1}$ with an extinction coefficient $\epsilon \sim 30\text{--}40$. In some high molecular weight hydrocarbons the low frequency band can be shielded by other absorptions. Of the two possible isomers the *trans* one has a slightly higher frequency than the *cis* isomer.

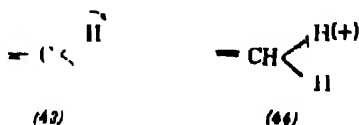
In trisubstituted ethylenes, the $\nu\text{C}-\text{H}$ band is very weak and difficult to identify. Tetrasubstituted ethylenes without hydrogen atoms at the double bond do not absorb in this region.

The position of the $\nu(-\text{CH})$ band in infrared spectra of alkenes depends on the inductive and conjugative effects of adjacent substituents (see dienes, α , β -unsaturated compounds, carbonyl compounds, carboxylic acids, halogen compounds, etc.).

In interpreting infrared spectra of alkenes, it has to be kept in mind that the $3000\text{--}3100\text{ cm}^{-1}$ region may contain bands arising from CH stretching vibrations of aromatic compounds, cyclopropanes, or poly-halogenated compounds with several halogen atoms attached to the same carbon. As in other cases, the assignment of a band in the region of stretching vibrations must be confirmed by the presence of characteristic bands in other spectral regions (in-plane or out-of-plane deformations, etc.).

c. **=C—H deformation vibrations.** Deformation vibrations of the unsaturated C—H bond have been extensively studied [124–127]. In ethylene, seven out of the twelve normal vibration modes are due to the deformation of =C—H bonds. In higher members of the series, the number and position of bands depend on the mode and extent of substitution at the double bond.

Each C—H bond of a double bond carbon atom can give rise to a deformation *in the plane of the double bond* (in-plane rocking) (43) and an *out-of-plane deformation* (perpendicular to the plane of the double bond) (44)



1. **In-plane deformation modes.** These modes have been less extensively studied. They are assigned the large spectral region between 800–1450 cm^{-1} [124–127]. On symmetry grounds the corresponding band is very weak or in certain cases, absent. Identification is difficult because the band occurs in the region associated with C—C stretching modes and with saturated C—H deformations. The assignment has to be enforced by bands in the region of —C—H and C—C stretching vibrations (3000–3100 cm^{-1} and 1600 cm^{-1} , respectively) and by the much more characteristic =C—H out-of-plane deformation mode (900–1000 cm^{-1}).

Monosubstituted ethylenes $\text{RCH}=\text{CH}_2$. The two types of C—H bonds of the vinyl group give rise to two in-plane deformation frequencies active both in the infrared and in Raman in the ranges 1410–1420 cm^{-1} and 1290–1300 cm^{-1} (see Table II-27). The higher frequency band is assigned

Table II-27 Frequency of in-plane deformation modes of CH bonds in 1-alkenes [127]

| Alkene | =CH ₂ deformation cm^{-1} | —CH— deformation cm^{-1} |
|-----------|--|--------------------------------------|
| Propene | 1416 | (1302) |
| Butene-1 | 1420 | 1297 |
| Pentene-1 | 1420 | (1300) |
| Hexene-1 | 1416 | 1297 |

Note: Values in parenthesis are uncertain.

1410–1420 cm^{-1} band is stronger and has a relatively constant position. It is of value for analytical purposes. The weaker band at ca. 1300 cm^{-1} is variable in position [127].

Asymmetrically disubstituted ethylenes $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$. These compounds have a single in-plane deformation band in the range 1410–1420 cm^{-1} (in isobutene, at 1420 cm^{-1}).

to the vibration of the =CH₂ group because it arises in asymmetrically disubstituted ethylenes as well. The lower frequency band is assigned to the vibration of the other CH bond of the vinyl group; it arises at about the same frequency on symmetrically disubstituted *cis* ethylenes. In propene, $\text{CH}_3\text{CH}=\text{CH}_2$, the frequencies of the two bands are 1416 and 1302 cm^{-1} . In spectra of compounds belonging to this series, the

Symmetrically disubstituted ethylenes $R_1CH=CHR_2$. For theoretical reasons the in-plane deformation vibration of the CH bond in symmetrically disubstituted *trans* ethylenes is forbidden in the infrared. Sometimes a weak band arises at $1290-1300\text{ cm}^{-1}$. In *cis* isomers, a medium intensity band at ca. 1105 cm^{-1} is assigned to this vibration (in 2-butene and 2-pentene, at 1406 cm^{-1} ; in 2-hexene at 1408 cm^{-1}). In Raman the band arises at $1255-1260\text{ cm}^{-1}$.

Trisubstituted ethylenes. These compounds have a single hydrogen atom at the C=C double bond. The =CH in-plane deformation band is very weak in the infrared, and in most cases it cannot be detected.

2. CH out-of-plane deformation vibrations. These vibrations give rise to the most characteristic absorptions in infrared spectra of alkenes [124-127]. The bands are of value for the determination of the number and position of hydrogen atoms at the C=C double bond and enable the identification of the mode and degree of substitution of this bond.

In **ethylene** the absorption occurs at 949 cm^{-1} and in **substituted ethylenes** within the range $600-1100\text{ cm}^{-1}$. The extinction coefficient of this band (50-150 units) can be twice or three times as large as that corresponding to similar deformation modes of CH bonds in alkanes (about 50 units). The band position varies widely with the structure in the vicinity of the bond. It is also dependent on the nature and number of substituents.

In unsaturated hydrocarbons where the substituent at the double bond is a nonplanar carbon atom of an alkyl group, CH out-of-plane deformations occur in the following regions [125, 126]:

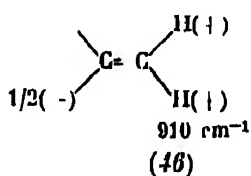
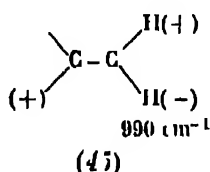


Monosubstituted ethylenes $\text{RCH}=\text{CH}_2$. The vinyl group has two absorption bands arising from out-of-plane deformation modes of CH bonds: one at ca. 990 cm^{-1} (Band I, Table II-28) and another at $\sim 910\text{ cm}^{-1}$ (Band II). Assignments of these bands raised many discussions [125–127]. The high

Table II-28 Out-of-plane deformation vibrations in monosubstituted ethylenes $\text{H}_2\text{C}=\text{CH}-\text{R}$ [126]

| Substituent R | Band I 990 cm^{-1} | Band II 910 cm^{-1} | Overtone | Substituent R | Band I 990 cm^{-1} | Band II 910 cm^{-1} | Overtone |
|------------------------------------|--------------------------------|---------------------------------|---------------|--------------------------|--------------------------------|---------------------------------|----------|
| Alkyl | 985 1000 | 905 912 | 1820— 1830 | OCH_3 | 960 | 813 | |
| $\text{CH}_3-\text{C}_6\text{H}_5$ | 989— 995 | 912— 915 | 1840 — | CH_3-Cl | 983 | 929 | 1861 |
| Aryl | 989 | 906 | 1815 | CH_3-Br | 981 | 924 | 1850 |
| $\text{CH}=\text{C}_6\text{H}_5$ | 1011 | 907 | 1819 | CHCl_2 | 975 | 937 | 1883 |
| $\text{C}=\text{C(H)}$ | 972 | 925 | 1850 | CF_3 | 979 | 965 | 1927 |
| I | 943 | 905 | — | CH_2OH | 987 | 915 | 1845 |
| Br | 936 | 898 | 1803 | CHO | 981 | 963 | 1941 |
| Cl | 938 | 894 | 1799 | COOR | 982 | 961 | 1928 |
| F | 925 | 863 | — | COOH | 982 | 970 | 1952 |
| | | | | $\text{C}\equiv\text{N}$ | 960 | 960 | 1920 |

frequency band at 990 cm^{-1} is assigned to the $-\text{CH}=\text{}$ deformation mode of carbon 2, while the 910 cm^{-1} band is assigned to the deformation mode of the $=\text{CH}_2$ group. In a different interpretation [126] based on analogy with vibrations of vinyl bromide, the 990 and 910 cm^{-1} bands are considered to be more complex vibration modes.



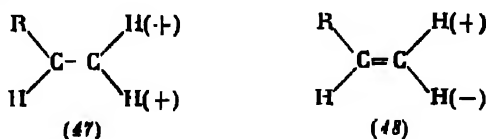
The 990 cm^{-1} frequency is assigned to a vibration similar to the deformation in disubstituted *trans* ethylenes, where a twisting of the $\text{C}=\text{C}$ bond takes place as well (45). The lower frequency (910 cm^{-1}) is assigned to the out-of-plane wagging of the $=\text{CH}_2$ group (46). A similar band occurs in spectra of compounds with a vinylidene group.

The band position at ca. 990 cm^{-1} varies with the nature of the substituent R (see Table II-28). In hydrocarbons ($\text{R}=\text{alkyl}$) the frequency falls within the range $985\text{--}1000\text{ cm}^{-1}$. It reaches the upper limit in compounds with branched alkyl radicals in the α -position. For example, *tert*-butylethylene (3,3-dimethylbutene-1) absorbs at 1000 cm^{-1} . In the homologous series of straight chain alkenes with a terminal double bond, the frequency variation does not exceed $\pm 3\text{ cm}^{-1}$.

The frequency decreases in compounds with vinyl groups directly linked to an electronegative atom or group. The largest effect is observed in vinyl halides, where the frequency decreases by 50–60 cm^{-1} cf. hydrocarbons. Vinyl bromide absorbs at 936 cm^{-1} whereas vinyl fluoride, with the lowest frequency absorbs at 925 cm^{-1} (in the vapor phase) [126]. In vinyl compounds with the vinyl group directly linked to an oxygen atom or to a polar group containing oxygen, the frequency decreases by 30–50 cm^{-1} . Functional groups containing nitrogen, lower the frequency by only 10–20 cm^{-1} . When the vinyl group is linked to an element with lower Pauling electronegativity than that of the alkyl group (e.g. Si), the frequency increases by ca. 20 cm^{-1} .

In alkylvinyl ethers, a doubling of this band is observed, dependent on the nature of the alkyl group. Alkylvinyl ethers with a primary alkyl group give rise to a band at 960 cm^{-1} with a shoulder at 943 cm^{-1} (methyl vinyl ether at 960 cm^{-1}). Alkyl vinyl ethers with secondary alkyls have two bands of equal intensity at 961 and 944 cm^{-1} and those with tertiary alkyls have a single band at 945 cm^{-1} (Table II-29). The splittings are thought to be due to conformational isomerism (see Band II).

The 910 cm^{-1} band (Band II, Table II-28) assigned to a wagging vibration of the CH_2 group ($\delta\text{CH}_2, w$) corresponds to the in-phase wagging of the two hydrogen atoms (47), perpendicular to the plane of the $\text{C}=\text{CH}_2$ bond [126]. The vibration is considered identical to that of asymmetrically disubstituted ethylenes. A different vibration mode, out-of-phase (48), does not change the dipole moment and consequently is inactive in the infrared:



The behavior of the in-phase deformation mode of the $=\text{CH}_2$ bond as a function of the nature of substituents is more complex.

In hydrocarbons with the vinyl group linked to a nonpolar carbon atom, the band occurs at 905–912 cm^{-1} [126] both in the case of saturated and unsaturated carbon atoms. Shifts are observed in some derivatives of styrene with bulky substituents in the ortho-position, for example, 2- or 2,6-dichlorostyrene absorbs at 930 cm^{-1} . This shift has been attributed to steric effects [126], since the conjugative effect in *p*-chlorostyrene acts in the opposite direction, resulting in a small shift towards lower frequencies. A small decrease in frequency is observed when the vinyl group is conjugated with $\text{C}=\text{C}$ or $\text{C}\equiv\text{C}$ bonds.

Comparative studies of a large number of vinyl compounds have shown that, except for hydrocarbons where the frequency is relatively constant, vinyl

Table II-29 Out-of-plane CH deformation frequencies in alkyl vinyl ethers [126]

| Alkyl vinyl ether | Band I, cm^{-1} | Band II, cm^{-1} |
|--|--------------------------|---------------------------|
| $\text{CH}_3-\text{O}-\text{CH}=\text{CH}_2$ | 960 | 813 |
| $\text{RCH}_2-\text{O}-\text{CH}=\text{CH}_2$ | 960 | 813, 825 |
| $\text{R}_2\text{CH}-\text{O}-\text{CH}=\text{CH}_2$ | 961, 944 | 810, 823 |
| $\text{R}_3\text{C}-\text{O}-\text{CH}=\text{CH}_2$ | 945 | 825 |

compounds substituted with different polar functional groups show large frequency variations in this region.

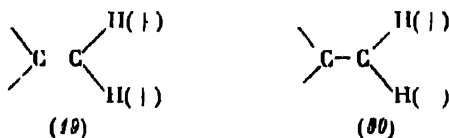
In compounds substituted in the allylic position with electronegative atoms or polar groups, $R-CHX-CH=CH_2$, the frequency varies within large limits with the nature of the substituent X. When $X=\text{halogen}$, the frequency increases by $15-20\text{ cm}^{-1}$ [126]. The effect seems to be additive. Allyl chloride absorbs at 929 cm^{-1} , while $Cl_2CH-CH=CH_2$ absorbs at 937 cm^{-1} . The trifluoromethyl group in $F_3C-CH=CH_2$ has the most powerful effect, increasing the frequency by ca. 50 cm^{-1} . In compounds substituted in the allylic position with an oxygenated functional group, the frequency increases by $5-25\text{ cm}^{-1}$, depending on the nature of the functional group.

In compounds with the vinyl group directly attached to an electronegative atom or group, the frequency decreases by $10-15\text{ cm}^{-1}$. An electropositive group increases the frequency by $50-60\text{ cm}^{-1}$. The groups $C=O$, $C\equiv N$, SO_2 , and NH_2 increase the frequency by $45-60\text{ cm}^{-1}$ [126, 128].

Vinyl ethers (Table II-29), $R-O-CH=CH_2$, have the lowest frequency ($813-825\text{ cm}^{-1}$). Methylvinyl ether has a single band at 813 cm^{-1} . *tert*-Alkylvinyl ethers have bands at 825 cm^{-1} . In vinyl ethers in which R is the primary alkyl two bands are assigned to this vibration: a strong one at ca. 813 and a weak one at 825 cm^{-1} . Vinyl ethers in which R is the secondary alkyl also have two bands in the same positions, but of equal intensities. The presence of two bands is due to conformational isomers [126, 128].

The first overtone of the out-of-plane, in-phase $=CH_2$ rocking vibration gives rise to strong absorptions at 1800 and 1910 cm^{-1} . In cases where it does not coincide with other strong fundamentals or overtones, it is a reliable diagnostic for this kind of vibration. The absence of this overtone shows beyond doubt that no vinyl group is present in the molecule.

Asymmetrically disubstituted ethylenes $R_1R_2C=CH_2$. These alkenes have an out-of-plane CH deformation band at ca. 890 cm^{-1} . The absorption is due to the out-of-plane, in-phase rocking vibration of the $=CH_2$ group (49).



The out-of-phase vibration (50) is inactive in the infrared. The electronic effects of substituents on this vibration mode are similar to those on the vinyl group. In this case also, the characteristic band of the overtone is observed in the $1785-1790\text{ cm}^{-1}$ region.

Table II-30 shows the characteristic frequencies of the out-of-plane $=CH_2$ deformation vibration of a series of compounds theoretically possible on asymmetrical disubstitution of ethylene.

In compounds with two nonpolar substituents, i.e., hydrocarbon groups, the frequency lies in the range $885-890\text{ cm}^{-1}$. Halogen atoms or electronega-

Table 11-30 Out-of-plane deformation vibration of the $=CH_2$ group in alkenes [126]

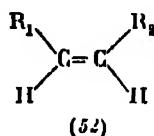
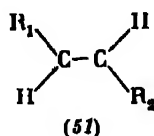
| Compound | Fundamental, cm^{-1} | Overtone, cm^{-1} | Compound | Fundamental, cm^{-1} | Overtone, cm^{-1} |
|---|---------------------------|------------------------|--|---------------------------|------------------------|
| $\begin{array}{c} R \\ \diagdown \\ C=CH_2 \\ \diagup \\ R \end{array}$ | 885-890 | 1785-1795 | $\begin{array}{c} Br \\ \diagdown \\ C-CH_2 \\ \diagup \\ I_3C \end{array}$ | 929 | — |
| $\begin{array}{c} CH_3 \\ \diagdown \\ C-CH_2 \\ \diagup \\ C_6H_5 \end{array}$ | 885-895 | 1785-1805 | $\begin{array}{c} CH_3 \\ \diagdown \\ C=CH_2 \\ \diagup \\ CH_3COO \end{array}$ | 869 | — |
| $\begin{array}{c} CH_3 \\ \diagdown \\ C-CH_2 \\ \diagup \\ ClCH_2 \end{array}$ | 902 | 1820 | $\begin{array}{c} CH_3 \\ \diagdown \\ C-CH_2 \\ \diagup \\ CH_3O \end{array}$ | 795 | 1600 |
| $\begin{array}{c} CH_3 \\ \diagdown \\ C-CH_2 \\ \diagup \\ Cl \end{array}$ | 875 | 1765 | $\begin{array}{c} C_2H_5O \\ \diagdown \\ C-CH_2 \\ \diagup \\ C_2H_5O' \end{array}$ | 711 | — |
| $\begin{array}{c} C_6H_5 \\ \diagdown \\ C-CH_2 \\ \diagup \\ Cl \end{array}$ | 877 | 1766 | $\begin{array}{c} CH_3 \\ \diagdown \\ C-CH_2 \\ \diagup \\ ROOC \end{array}$ | 959 | 1882 |
| $\begin{array}{c} Cl \\ \diagdown \\ C=CH_2 \\ \diagup \\ Cl \end{array}$ | 867 | 1744 | $\begin{array}{c} CH_3 \\ \diagdown \\ C-CH_2 \\ \diagup \\ HOOC \end{array}$ | 917 | 1905 |
| $\begin{array}{c} Br \\ \diagdown \\ C-CH_2 \\ \diagup \\ Br \end{array}$ | 877 | 1765 | $\begin{array}{c} CH_3 \\ \diagdown \\ C=CH_2 \\ \diagup \\ RCO \end{array}$ | 930 | 1865 |
| $\begin{array}{c} F \\ \diagdown \\ C-CH_2 \\ \diagup \\ F \end{array}$ | 801 | 1613 vapor | $\begin{array}{c} CH_3 \\ \diagdown \\ C-CH_2 \\ \diagup \\ NC \end{array}$ | 930 | 1878 |
| $\begin{array}{c} Br \\ \diagdown \\ C-CH_2 \\ \diagup \\ BrCH_2 \end{array}$ | 896 | 1802 | $\begin{array}{c} NC \\ \diagdown \\ C=CH_2 \\ \diagup \\ NC \end{array}$ | 985 | 1970 |

R - alkyl

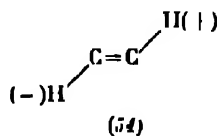
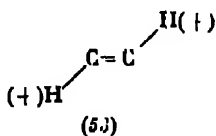
tive groups in the allylic position (α to the vinyl group) *increase* the frequency by 5–25 cm^{-1} cf. the corresponding hydrocarbons. However, when the halogen atom is directly attached to the vinylidene group, the $=\text{CH}_2$ deformation frequency *decreases* by ca. 10 cm^{-1} . Two chlorine atoms decrease the frequency by ca. 20 cm^{-1} , two bromine atoms by 10 cm^{-1} , and two fluorine atoms by as much as 80 cm^{-1} . The effect of the allylic halogen and the vinylic halogen directly attached to the carbon atom of the double bond seem to compensate each other in $\text{F}_3\text{C}-\text{CBr}=\text{CH}_2$, where the increase in frequency is only ca. 40 cm^{-1} .

The $\text{C}=\text{O}$ group has the same effect as the vinyl group and increases the frequency by ca. 40 cm^{-1} cf. hydrocarbons. In esters the increase in frequency is ca. 50 cm^{-1} , and in acids, ca. 55 cm^{-1} [126].

Symmetrically disubstituted ethylenes. The absorption band corresponding to the out-of-plane deformation vibration of the two hydrogen atoms of symmetrically disubstituted ethylenes is currently used to distinguish between *cis* and *trans* isomers. In the *trans* forms (51) of hydrocarbons ($\text{R}=\text{alkyl}$), the absorption is strong and occurs at ca. 970 cm^{-1} . In *cis* forms (52), the band is very weak or absent [125, 126, 129–131]:



trans Isomers. Of the two possible vibration modes for the *trans* configuration only the first one is active in the infrared.



This vibration mode implies a corresponding twisting of the $\text{C}=\text{C}$ bond and gives rise to a strong absorption in the range 965–990 cm^{-1} [126]. The frequency of this vibration varies very little with the length of the hydrocarbon group R attached to the double bond. However, the intensity of the band varies inversely with the molecular weight of R . Since it is not influenced by the nature of substituents, this band is of value to confirm the *trans* structure of the alkene. Its absence shows beyond doubt the absence of a *trans* configuration. Since this band occurs in a crowded region, its assignment has to be confirmed by other characteristic regions ($=\text{CH}$ and $\text{C}=\text{C}$). The band is of value in quantitative determinations as well. Its intensity in *trans* alkenes is ca. 145 units. It should be pointed out that additive intensity meas-

measurements may be of use in determining the ratio of double bonds in chains and thus the degree of unsaturation in acids, terpenoids, carotenoids, etc., as well as in monitoring polymerization reactions of styrene, butadiene, etc.

=CH out-of-plane deformation frequencies for several *cis* and *trans* alkenes and for *trans* disubstituted ethylenes are shown in Tables II-31 and II-32, respectively.

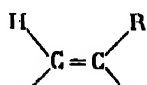
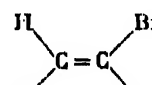
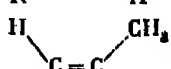
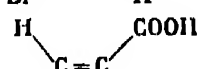


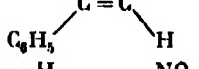
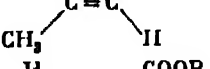
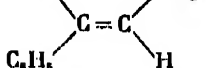
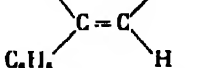
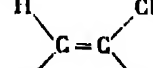
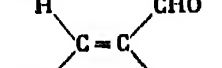
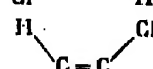
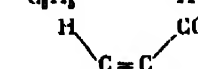
cis Isomers have the out-of-plane deformation band at 675—725 cm^{-1} [125, 127]. This band is variable in position and its assignment is unreliable since it can easily be mistaken for other bands in this region.

Trisubstituted ethylenes $\text{R}_1\text{R}_2\text{C}=\text{CHR}_3$. The out-of-plane deformation vibration of the single hydrogen at the double bond in trisubstituted

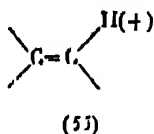
Table II-31 =CH out-of-plane deformation frequencies in *cis* and *trans* alkenes [126]

| Alkene | <i>cis</i> Isomer cm^{-1} | <i>trans</i> Isomer cm^{-1} |
|-----------------------------|---------------------------------------|---|
| Butene-2 | 675 | 964 |
| Pentene-2 | 696 | 964 |
| Hexene-2 | 694 | 906 |
| Hexene-3 | 714 | 965 |
| 2,2,5,5-Tetramethylhexene-3 | — | 978 |

Table II-32 Out-of-plane deformation frequencies in disubstituted ethylenes [126]

| Formula | Frequency cm^{-1} | Formula | Frequency cm^{-1} |
|---|-------------------------------|---|-------------------------------|
|  | 962—966 |  | 896 |
|  | 959 |  | 966 |
|  | 958 |  | 968 |
|  | 964—967 |  | 972 (shoulder at 983) |
|  | 931 |  | 972 |
|  | 892 |  | 976 |
|  | |  | |

ethylenes is a rocking above and below the plane of the bond (55):



In hydrocarbons the frequency of this vibration lies within the range 800–840 cm^{-1} [121]. The specificity of this vibration is less than in previous cases. The band may be used to distinguish between trisubstituted alkenes, $\text{R}_1\text{R}_2\text{C}=\text{CHR}_3$, and tetrasubstituted ones, $\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4$ [132, 133].

The overtone of this band (800–840 cm^{-1}) occurs at 1600–1680 cm^{-1} [126, 127].

The band is variable in position, depending to a great extent on the nature of substituents when R is not a hydrocarbon group. Polar substituents give rise to larger shifts than in mono- and disubstituted ethylenes.

3. *Other vibrations in alkenes.* Tetrasubstituted ethylenes, $\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4$, where one of the substituents is a CH_3 group, give rise to a band at 1155 cm^{-1} , assigned to the $\text{CH}_3-\text{C}=\text{C}$ unit [133]

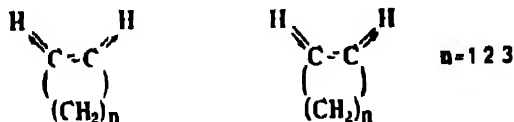
The vibration of CH_2 and CH_3 groups from the saturated part of the molecule is affected only if they are adjacent to the double bond. The effect results in a decrease in deformation frequencies arising from these groups. In the case of δCH_2 and δCH_3 bands at 1450–1475 cm^{-1} inflections, occur at 1430–1450 cm^{-1} .

The band arising from the symmetrical stretching mode of the CH_3 group is a doublet due to a resonance effect, but the mean value remains 2872 cm^{-1} [134].

2. Cycloalkenes

a. Monocyclic alkenes

The double bond in cycloalkenes corresponds to the *cis* symmetrically disubstituted ethylene type (see Table II-21). $\text{C}=\text{C}$ and $\text{C}=\text{H}$ bonds give



rise to normal vibration modes. However, the frequency and intensity of absorption bands varies with ring size.

a. **C=C stretching vibration.** The normal frequency of the C=C stretching vibration in *cis*-alkenes is 1650 cm^{-1} . In six-, seven-, and eight-membered ring alkenes, the frequencies are very close to this value (see Table II-33).

Table II-33 $\nu\text{C}=\text{C}$ and $\nu=\text{CH}_2$ frequencies in cycloalkenes, cm^{-1} [135]

| Cycloalkene | $\nu\text{C}=\text{C}$ | $\frac{\nu}{\text{cm}}$ $\frac{\text{CH}_2}{\text{cm}}$ | | $\nu\text{C}=\text{CH}_2$ (exocyclic) |
|-------------------------|------------------------|---|------|--|
| Cyclopropene | 1641 | 3070 | — | 1730 |
| Cyclobutene | 1566 | 3048 | 3126 | 1678 |
| Cyclopentene | 1611 | 3061 | — | 1657 (R)* |
| Cyclohexene | 1649 | 3024 | 3067 | 1651 (R) |
| Cycloheptene | 1650 | 3020 | 3059 | — |
| <i>cis</i> -Cyclooctene | 1648 | 3010 | 3053 | — |
| <i>cis</i> -Butene-2 | 1658 | 3023 | — | 1654 |

* R — active in Raman.

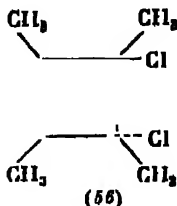
Cyclohexene absorbs at 1649 cm^{-1} and *cis* cyclooctene at 1648 cm^{-1} [135]. In cyclopentene the frequency falls to 1611 cm^{-1} . The behavior of three- and four-membered rings is interesting. The frequency in cyclopropene is close to normal, 1641 cm^{-1} ; however, in cyclobutene it falls to 1566 cm^{-1} [136]. According to the classical strain theory, one would expect the lowest frequency to occur in the three-membered ring; hence an "abnormal" value occurs in cyclobutene. The decrease in frequency is due to a decrease in force constant, and as a result the C=C distance becomes longer than 1.33 \AA in the molecule of cyclobutene [136]. The phenomenon can be rationalized on the basis of the special character of C=C bonds and of possible transannular interactions. In the cycloalkane series cyclobutane also shows special behavior (see page 155).

Variation of $\nu\text{C}=\text{C}$ band intensities with ring size is also interesting. The intensity increases in going from cyclooctene to cyclohexene. It is the same in cyclohexene as in cyclopentene but decreases in cyclobutene; in cyclopropene it has the same value as in cyclopentene. These observations again point out the different behavior of bonds in the four membered ring as well as the influence due to changes in bond angles.

In compounds with cyclopropene rings, weak bands at higher frequencies are observed; for example, sterculic acid gives rise to a band at 1865 cm^{-1} [137] assigned to the $\nu\text{C}=\text{C}$ vibration while 1,2-dimethylcyclopropene absorbs at 1898 cm^{-1} [138]. It is apparent that alkyl groups strongly affect the vibration of this bond.

An analogous effect is observed in methylcyclobutenes. In tetramethyl-3,4-dichlorocyclobutene (56), the $\nu\text{C}=\text{C}$ frequency occurs at 1684 cm^{-1} . The

same frequency is observed in *syn* and *anti* dimers of tetramethylcyclobutadiene (see page 185).



An appreciable increase in $\nu\text{C}=\text{C}$ frequency is observed in strain-free methylcycloalkenes [140]. In 1-methylcyclopentene the double bond frequency occurs at 1658 cm^{-1} , cf. 1611 cm^{-1} in cyclopentene; in methylcyclohexene it occurs at 1674 cm^{-1} cf. 1649 cm^{-1} in cyclohexene. 1-Butylcycloheptene absorbs at 1673 cm^{-1} [140], and a series of alkylcycloheptenes with $\text{R}=\text{CH}_3$, C_2H_5 , C_3H_7 , C_4H_9 absorb at 1670 cm^{-1} [141, 142].

The influence of other substituents will be discussed in subsequent chapters (Halogen Compounds, Carboxylic Acids etc.).

b. $=\text{C}-\text{H}$ stretching vibrations. The frequency of the $=\text{C}-\text{H}$ stretching vibration increases with decreasing ring size. In the series cyclohexene, cyclopentene, cyclobutene, the frequency increases from 3017 cm^{-1} in cyclohexene to 3045 cm^{-1} in cyclopentene and 3060 cm^{-1} in cyclobutene [140, 143]. The change in frequency of the $\text{C}=\text{C}$ and $=\text{C}-\text{H}$ stretching vibrations with the number of ring carbon atoms has been used extensively to determine the size of the ring (see an example on page 184).

High resolution equipment enables the identification of the two $=\text{C}-\text{H}$ stretching modes: the symmetric mode arising at lower frequency and the asymmetric mode at higher frequency. In Table II-33 are shown the frequencies of $\nu(=\text{CH})$ sym and $\nu(=\text{CH})$ asym modes for the homologous series of cycloalkenes from cyclopropene to cyclooctene. The frequencies of *cis* butene-2 [135] are given for comparison. The low frequency, generally stronger bands are assigned to the symmetrical vibration. The bands arising from asymmetrical vibrations have higher frequencies and are very weak. They are hardly noticeable in cyclopentene and cyclopropene [135]. The symmetrical vibration is less sensitive to ring size vibration; the asymmetrical vibration seems to vary in a more characteristic way although in some cases the positions are not certain.

c. CH_2 stretching vibrations. The frequencies of CH_2 stretching vibrations in cycloalkenes are comparable to those in aliphatic compounds [144]. Cyclohexene absorbs at 2851 and 2927 cm^{-1} and cyclopentene at 2853 and 2959 cm^{-1} .

d. CH_2 deformation vibrations. In cycloalkenes the δCH_2 vibration modes arise at lower frequencies than in straight chain alkanes [145, 146]. Cyclohexene has a single band at 1450 cm^{-1} . *cis*-Cyclooctene and *cis*-cyclodecene have two bands, 1465 and 1450 cm^{-1} . *trans*-Cyclooctene and *trans*-cyclodecene have only the 1450 cm^{-1} band [145].

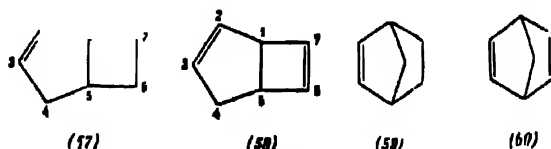
b. *Bi- and polycyclic alkenes*

Generally, the stretching vibrations of $C=C$ and $=C-H$ bonds in bi- and polycyclic alkenes are $10-10\text{ cm}^{-1}$ lower than in monocyclic alkenes [135]. The strained bridgehead $C-H$ bonds show different behavior (see page 163).

Some bi- and polycyclic systems are described below.

Bicyclo [3. 2. 0] heptene-2 (57) has the double bond frequency at 1605 cm^{-1} , close to that of cyclopentene (1611 cm^{-1}) [147].

Bicyclo [3. 2. 0] heptadiene 2,6 (58) has two absorptions in the $C=C$ stretching mode region: 1557 and 1605 cm^{-1} . It should be pointed out that these bands have frequencies corresponding to those of condensed five- and four-membered rings, respectively. The separate occurrence of these absorptions shows that the mechanical interaction between the two vibration modes is very weak [147].



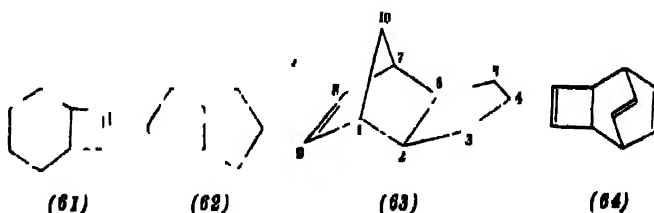
Bicyclo [2. 2. 1] heptene-2 (59) and bicyclo [2.2.1] heptadiene 2,5 (60) show some characteristic features. In the former, the $\nu_{C=C}$ frequency falls to 1568 cm^{-1} cf. 1611 cm^{-1} in cyclopentene [148, 149].

The more strained bicyclo [2.2.1] heptadiene -2,5 (60) absorbs at 1550 cm^{-1} . The frequencies in these systems are close to those in cyclobutene or in condensed systems with cyclobutene rings.

Bicyclo [4. 2. 0] octene-7 (61) has the $\nu_{C=C}$ frequency of the four-membered ring at 1560 cm^{-1} [147].

Bicyclo [3. 3. 0] octene-2 (62) gives rise to a band at 1617 cm^{-1} , corresponding to the $C=C$ stretching vibration in the strain-free, five-membered ring.

Tricyclo [5. 2. 1. 0^{2,4}] decadiene-3,8 (dicyclopentadiene) (63) has two $\nu_{C=C}$ vibrations: 1560 and 1640 cm^{-1} . The frequency at 1560 cm^{-1} corresponds to the 8,9-bond of the bicycloheptene ring and that at 1640 cm^{-1} , to the 3,4- bond of the cyclopentene ring [150].



Tricyclo [4.2.2.0^{2,5}] *decaltriene*-3, 7, 9 (64) has two double bonds in the bicyclooctadiene ring and one double bond in the fourmembered ring. The spectrum shows two bands (Fig. II-36) of medium intensity, one at 1560 cm⁻¹ (probably arising from the cyclobutene ring) and the other at 1590 cm⁻¹ [151]. The bands disappear on complexing with PdCl₂.

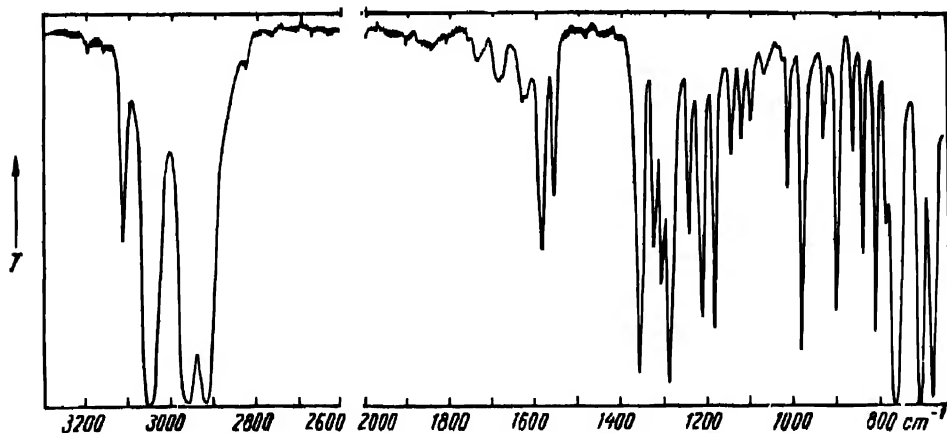
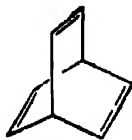


Fig. II 36 Infrared spectrum of tricyclo [4.2.2.0^{2,5}] decatriene-3,7,9, [118]

being replaced by two bands at 1412 and 1480 cm⁻¹ (this region is characteristic for double bonds complexed with Pd [149, 152]).

=C-H bonds absorb at 3055 and 3105 cm⁻¹, and saturated CH bonds absorb at 2920 and 2962 cm⁻¹.

Bicyclo [2.2.2] *octatriene*-2, 5, 7 (*barelene*) (65) has a strong band in the double bond region at 1577 cm⁻¹ and a weaker one at 1613 cm⁻¹. The C-H frequencies arise at 3040 cm⁻¹ for =C-H bonds and at 2950 cm⁻¹ for bridgehead >C-H bonds [153].



(65)

Tricyclo [4.2.0.0^{2,5}] *octadiene*-3, 7 is the dimer of cyclobutadiene, consisting of three condensed four-membered rings which can have a *syn* (66) or *anti* (67) configuration. The double bond frequency of the cyclobutene rings is close to that of cyclobutene: 1515 cm⁻¹ in the *syn* stereoisomer and 1555 cm⁻¹ in the *anti* isomer [154, 155] (Fig. II-37).

Octamethyltricyclo [4.2.0.0^{2,5}] octadiene (the *syn* and *anti* dimers of tetramethylcyclobutadiene) [139, 156] have $\nu_{C=C}$

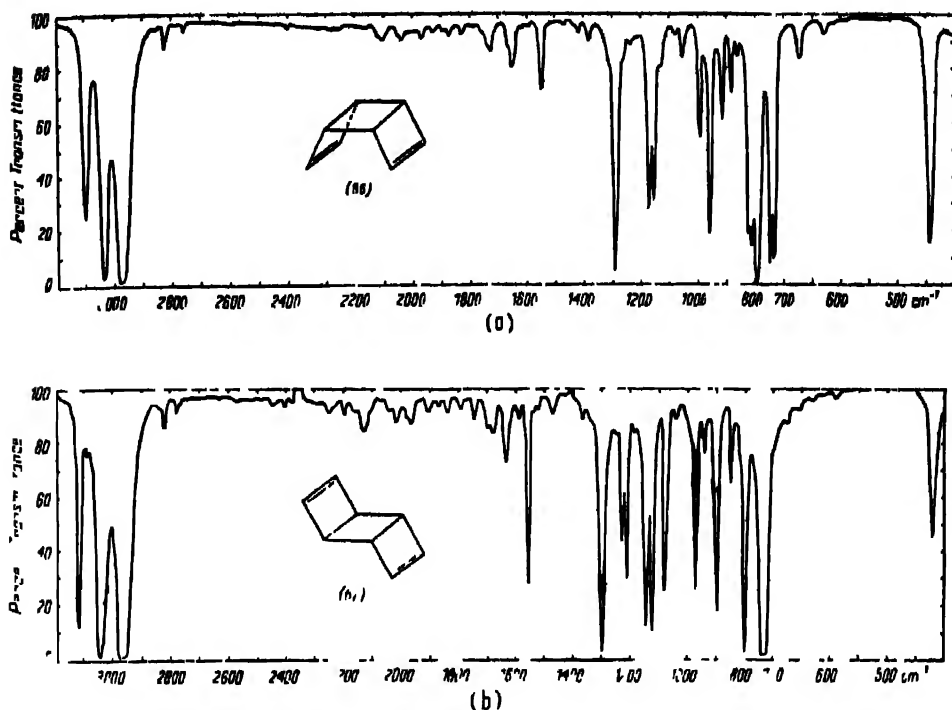
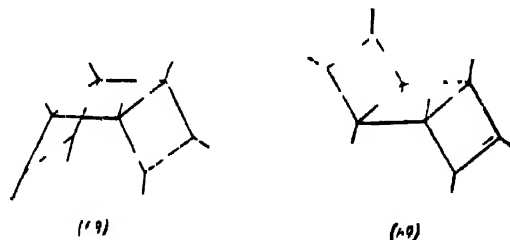


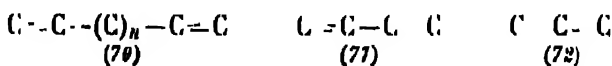
Fig. 11-37 Infrared spectrum of tricyclo [4.2.0.0^{2,5}] octadiene-2, 7:
(a) *syn* form (66); (b) *anti* form (67).

frequencies at 1684 cm^{-1} in the *syn* isomer (66) and 1681 cm^{-1} in the *anti* isomer (67).



3. Unsaturated hydrocarbons with multiple double bonds

Double bonds in dienes can be isolated (70), conjugated (71), or cumulated (72):



The mutual influence of the double bonds is stronger the closer they are to each other. In compounds with isolated double bonds, this influence is practically negligible.

From the vibrational point of view, *alkenes with isolated double bonds* have the same behavior as those with a single double bond. Because of additivity, band intensity increases with the number of double bonds in the molecule.

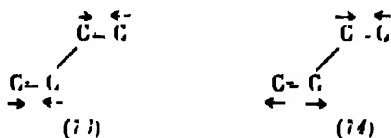
a. Alkenes with conjugated double bonds

Dienes and polyenes with conjugated double bonds show characteristic frequency shifts when compared to alkenes with a single double bond.

Quantum-mechanical interactions between π -electrons of the conjugated system decrease the C=C double bond order and increase the simple C—C bond order [157].

Absorption bands of individual double bonds cannot be identified separately, and the C=C—C=C system behaves like a vibrational entity. Consequently, a butadiene-type conjugated system has the following characteristic vibrational modes [158–161]: C=C stretching vibrations in the 1600 cm^{-1} region, =C—H stretching vibrations in the 3000 cm^{-1} region, and unsaturated and saturated C—H deformation vibrations in the 1000 cm^{-1} region.

a. **C=C stretching vibrations.** In dienes and polyenes vibrations of conjugated double bonds are strongly coupled to each other. In *trans*-2,3-dimethylbutadiene, the carbon atoms of the two double bonds vibrate in-phase (symmetrically) (73) or in opposite-phase (asymmetrically) (74) [159, 160]. The frequency of these coupled vibrations is lower than those of isolated double bonds. In molecules with a center of symmetry,



only the asymmetrical vibration is active in the infrared. In 2,3-dimethylbutadiene, the absorption occurs at 1600 cm^{-1} . The symmetrical vibration is active in Raman (1635 cm^{-1}). In butadiene the vibration is forbidden in the infrared. The infrared and Raman spectra of butadiene support the *s-trans* configuration of the molecule [162]. This structure is supported by the electron diffraction method as well [157, 163]. The two coupled $\nu_{\text{C}=\text{C}}$ vibration modes active in Raman give rise to frequencies at 1613 and 1599 cm^{-1} .

By reducing the symmetry (e.g., in 2-alkylbutadiene-1,3) the vibrations become active both in the infrared and Raman. In the infrared spectrum two bands occur in the double bond region, 1600 and 1635 cm^{-1} . The asymmetrical vibration band is much stronger and is shifted by ca. $30\text{--}40\text{ cm}^{-1}$ towards lower frequency cf. the corresponding monoalkene [158]. The second band is weaker.

For a series of 2-alkylbutadienes-1, 3 [164], the frequencies of asymmetrical vibrations are shown in Table II-34.

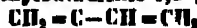
The intensity of the band corresponding to the $\nu\text{C}=\text{C}$ symmetrical vibration increases with the size of the alkyl group in the 2-position.

In polyenes the number of bands in the $1600\text{--}1650\text{ cm}^{-1}$ region increases with the number of double bonds. In the $\text{CH}_3(\text{CH}=\text{CH})_n\text{CH}_3$ series with $n=2, 3, 4$, the strongest band has a frequency of ca. 1650 cm^{-1} .

Although no correlation could be established between the number of bands, their frequency, and the number of conjugated double bonds, it was shown empirically that dienes, trienes, and tetraenes have two, three, and four bands, respectively in this region [165].

The number of $\nu\text{C}=\text{C}$ bands active in the infrared depends on the geometrical configuration of the molecule. The double bonds can adopt a *trans-trans* (75), a *cis-cis* (76), or a *trans-cis* (77) configuration.

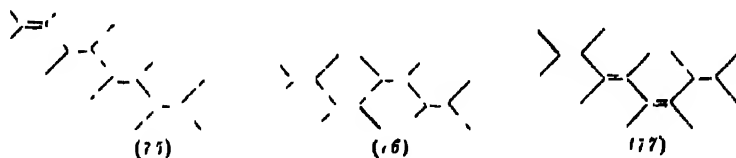
Table II-34 $\nu\text{C}=\text{C}$ frequencies in 2-alkylbutadienes-1,3 [164]



R

| R | $\nu\text{C}=\text{C}$ sym, cm^{-1} | $\nu\text{C}=\text{C}$ asym, cm^{-1} |
|---|--|---|
| CH_3 | 1642 w | 1595 s |
| CH_2CH_2- | 1633 w | 1590 s |
| $(\text{CH}_2)_3\text{CH}$ | 1632 | 1590 |
| $(\text{CH}_2)_3\text{C}-$ (<i>cis</i>) | 1611 w | 1645 |
| $(\text{CH}_2)_3\text{C}-$ (<i>trans</i>) | 1635 | 1595 s |
| $(\text{CH}_2)_3\text{C}-\text{CH}_2-$ | 1642 w | 1596 s |

Note. w - weak; s = strong.



The vibrational analysis of some tri- and tetraenes was used in assigning the geometrical configurations of these molecules. Of the six possible geometrical isomers in 1, 3, 5-hexatriene [166], the *trans-trans* form can have a single $\nu\text{C}=\text{C}$ vibration active in the infrared. It was assigned the strong doublet at $1623\text{--}1632\text{ cm}^{-1}$. Two weak bands arising at 1592 and 1675 cm^{-1} are due to combinations of low frequency vibrations. The *cis* isomers have three $\nu\text{C}=\text{C}$ bands. 2, 4, 6-Octatriene [166] absorbs at 1601 , 1644 , and 1685 cm^{-1} . The spectrum of 1, 3, 5, 7-octatetraene [161] corresponds to the *trans-trans* configuration (75) (C_{2h}). The strong band at 1631 cm^{-1} was assigned to $\nu\text{C}=\text{C}$ vibrations (see Table II-35).

Diene-yne conjugation decreases the frequency by $30\text{--}35\text{ cm}^{-1}$. Vinylacetylene absorbs at 1600 cm^{-1} [160].

b. $=\text{C}-\text{H}$ stretching vibration. In 1, 3-butadiene [166, 167], the $\text{C}-\text{H}$ asymmetrical vibration of the $=\text{CH}_2$ group occurs at 3100 cm^{-1} (in monoalkenes it falls in the range $3075\text{--}3095\text{ cm}^{-1}$). In 1, 3, 5-hexatriene, it

Table 11-15 Characteristic frequencies of di- and polyenes [161]

| Type of vibration | | | | | | Group frequency in monoalkenes |
|----------------------------------|--------|------|------|------|------|--------------------------------|
| Stretching | | | | | | |
| CH ₂ asym | 3105.5 | 3090 | 3100 | 3091 | 3070 | 3075-3095 |
| CH ₂ sym | 2989 | 2991 | 3000 | 2953 | 2955 | |
| CH vinyl | | 3013 | 3060 | 3010 | 3009 | 3010-3040 |
| CH <i>trans</i> -alkene | | | | 3012 | 2988 | 3010-3040 |
| C=C sym | | 1652 | | 1623 | 1631 | 1640-1680 |
| C-C asym | | | | | | |
| Deformation | | | | | | |
| CH ₂ | 1444 | 1419 | 1481 | 1413 | 1405 | 1410-1420 |
| CH ₂ vinyl | | | | 1291 | 1279 | 1290-1310 |
| CH ₂ in-plane rocking | | 1229 | 1290 | 1255 | 1229 | |
| in-plane CH <i>trans</i> | | | | 1166 | 1179 | 1295-1310 |
| out-of-plane CH vinyl | | | | 1011 | 1007 | 985-995 |
| CH <i>trans</i> -alkene | | | | 941 | 951 | 960-970 |
| CH ₂ in-phase | 949 | 912 | 911 | 899 | 897 | 905-915 |
| CH ₂ <i>t</i> | | 578 | 520 | 658 | 816 | |

occurs at 3092-3102 cm⁻¹ (doublet) and in 1, 3, 5, 7-octatetraene at 3070 cm⁻¹ [166].

The symmetric ν C-H stretching vibration of the CH₂ group in 1, 3-butadiene has a frequency of 3000 cm⁻¹. In 1, 3, 5-hexatriene it is assigned the 2955 cm⁻¹ band [166, 167].

In the *trans-trans* structure (75), the vibration of the vinylic CH bond has a higher frequency than that of internal *trans* bonds in alkenes. In butadiene the band arising from the vinylic CH bond occurs at 3060 cm⁻¹. In 1, 3, 5-hexatriene and 1, 3, 5, 7-octatetraene, it occurs at 3010 and 3009 cm⁻¹, respectively [166, 167]. The 3012 cm⁻¹ band in the spectrum of 1, 3, 5-hexatriene and the 2988 cm⁻¹ band in the spectrum of 1, 3, 5, 7-octatetraene were assigned to the stretching vibrations of the *trans*-alkenic CH bonds.

c. =C-H deformation vibrations. The in-phase, out-of-plane deformation vibration of terminal -CH₂ groups gives rise to a band at 911 cm⁻¹ in butadiene, at 899 cm⁻¹ in 1, 3, 5-hexatriene, and at 897 cm⁻¹ in 1, 3, 5, 7-octatetraene.

The out-of-plane deformation vibration of =C-H bonds (960-970 cm⁻¹ in alkenes) varies with the geometrical configuration of the di- or polyenic system -CH=CH-CH=CH- [161, 166, 167]. In *trans-trans* isomers both the frequency and the intensity of the band decrease [166, 168]. The *trans* isomer of 1, 3-pentadiene [169] and of 1, 4-diacetyl-1, 3-butadiene [170] give rise to bands at 949 and 945 cm⁻¹, respectively which are of less than

medium intensity. The *cis-cis* isomers show no absorption in this region; however, they have strong bands in the range $960\text{--}970\text{ cm}^{-1}$ [170]. *cis-trans* isomers have a band between $930\text{--}950\text{ cm}^{-1}$ [161]. 1, 3, 5-Hexatriene and 1, 3, 5, 7-octatetraene absorb at 941 and 951 cm^{-1} , respectively, corresponding to the *trans-trans* configuration [161, 166]. The vinylic $=\text{C-H}$ out-of-plane vibration has a frequency of $1010 \pm 2\text{ cm}^{-1}$.

In Table II-35, characteristic frequencies of a number of di- and polyalkenes are compared to the corresponding frequencies in ethylene and propene (last column).

b. Cyclic dienes and polyenes

Cyclopentadiene [171, 172] in the liquid state or in solution (Fig. II-38) gives rise to four bands in the CH stretching vibrations region at 3040 , 3071 , 3100 , and 3150 cm^{-1} . The bands at 1600 and 1638 cm^{-1} were assigned to the $\nu\text{C}=\text{C}$ vibration.

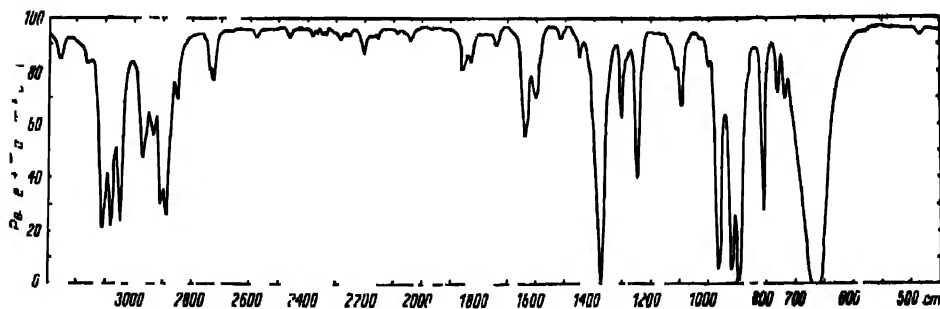


Fig. II-38 Infrared spectrum of cyclopentadiene (liquid film)

1, 3-*Cyclohexadiene* [173] has two medium intensity bands in the $\text{C}=\text{C}$ stretching vibration region 1580 and 1610 cm^{-1} , and four strong bands in the CH vibrations region: 2830 , 2880 , 2940 , and 3040 cm^{-1} (Fig. II-39).

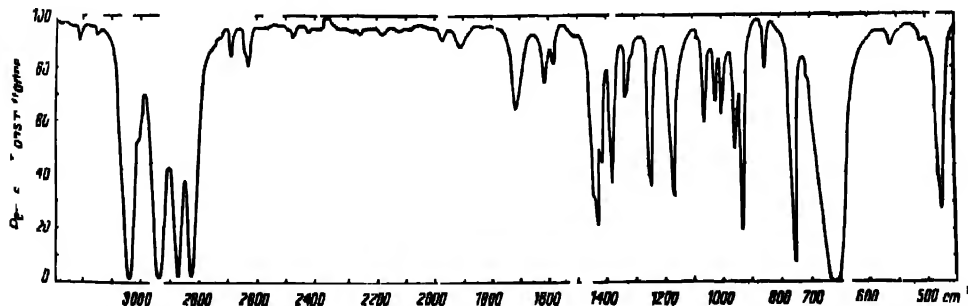
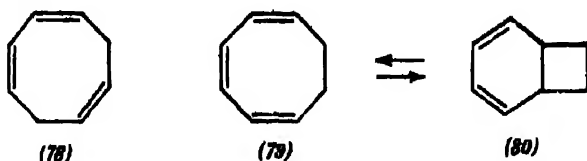


Fig. II-39 Infrared spectrum of cyclohexadiene (liquid film).

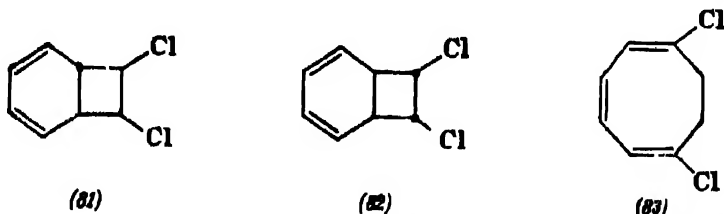
1,3,5- and 1,3,6-Cyclooctatrienes are obtained by reduction of cyclooctatetraene [174].



1, 3, 6-Cyclooctatriene (78) has two conjugated double bonds and an isolated double bond. The frequency of the latter is 1652 cm^{-1} . The conjugated double bonds have a strong absorption in Raman at 1620 cm^{-1} .

1, 3, 5-Cyclooctatriene (79) is in dynamic equilibrium with bicyclo [4.2.0] octadiene-2, 4 (80) [175]. The double bond region [176] has two medium intensity bands, 1610 and 1638 cm^{-1} , and a weak band at 1680 cm^{-1} . The stretching vibration of the alkenic C-H bond occurs at 3010 cm^{-1} .

Bicyclo [1.2.0] octadiene-2, 1 (80) absorbs at 1579 , 1645 and 1710 cm^{-1} .



7, 8-*trans*-Dichlorobicyclo [4.2.0] octadiene-2, 4 (81) has a strong absorption at 1586 cm^{-1} . Two more bands occur in the spectrum at 1683 and 1737 cm^{-1} . The strong band at 3035 cm^{-1} is assigned to the stretching vibrations of the alkenic C-H bonds [176,177]. In the *cis* isomer (82), the $\nu\text{C}=\text{C}$ and $\nu\text{C}-\text{H}$ regions of the spectrum remain unchanged.

1, 6-Dichlorocyclooctatriene-1, 3, 5 (83) with three conjugated double bonds has the $\nu\text{C}=\text{C}$ frequency at 1610 and 1637 cm^{-1} , the same as 1, 3, 5-cyclooctatriene [176, 177].

The δCH_2 band arises at 1435 cm^{-1} ($\nu\text{C}-\text{Cl}=859\text{ cm}^{-1}$).

The infrared spectra of cyclooctatetraene and deuterocyclooctatetraene (C_8D_8) support both the crown conformation with D_4 symmetry (84) and the boat conformation (85) with D_{2d} symmetry [178].

The simplicity of the spectrum of cyclooctatetraene shows that the molecule has a high degree of symmetry and rules out the possibility of an equilibrium between several conformations. It was shown recently that in the liquid state the bicyclic isomer (86) is present in the ratio 0.01 %, in equilibrium with the monocyclic form. However, it cannot be detected in the infra-



red [179]. The infrared spectrum of the bicyclic isomer (86), recorded at -20°C , has the $\nu\text{C}=\text{C}$ frequency at 1552 cm^{-1} and the νCH frequency at 3112 cm^{-1} [179a]. The boat conformation of cyclooctatetraene with D_{2d} symmetry is supported by X-ray analysis, electron diffraction and n.m.r. [179b].

The $\nu\text{C}=\text{C}$ bands (Fig. II-40) occur at 1655 cm^{-1} , the νCH bands at 2950 and 3010 cm^{-1} , and the deformation mode bands at 805 cm^{-1} .

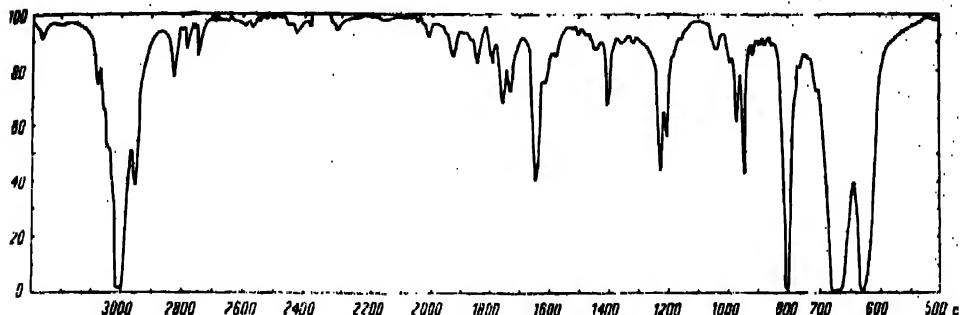


Fig. II-40 Infrared spectrum of cyclooctatetraene (liquid film).



(87)

cis, cis, cis-Cyclononatriene-1, 4, 7 (87) with a 6π homoconjugated system [180] shows the frequencies of *cis*-alkenes. The νCH bands occur at 3018 , 2965 , 2932 , 2916 , and 2864 cm^{-1} . The $\nu\text{C}=\text{C}$ vibration gives rise to very weak bands at 1676 and 1641 cm^{-1} . The CH out-of-plane deformation vibration has a frequency of 717 cm^{-1} .

c. Fulvenes

Fulvenes have characteristic absorptions in the 1600 cm^{-1} region ($\nu\text{C}=\text{C}$ vibrations); in the 1360 cm^{-1} region (vibrations arising from the fulvenic ring); and in the 750 cm^{-1} region (CH out-of-plane deformations) [181].

1. 1600 cm^{-1} region. All fulvenes (88) give rise to a strong absorption band at ca. 1600 cm^{-1} (Table II-36). The high intensity of this band is due to the dipolar structure (89) of the exocyclic bond [182].

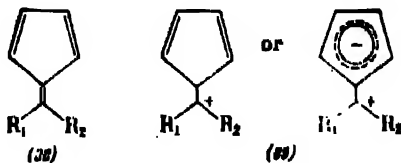
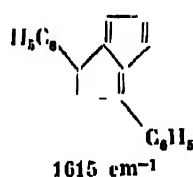
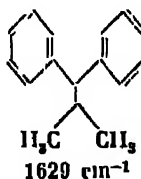
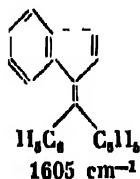
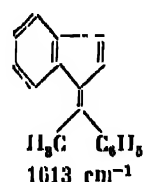
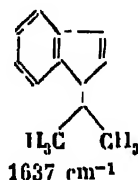
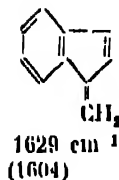
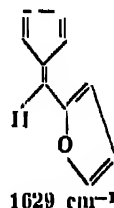
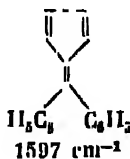
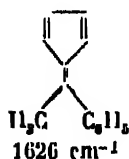
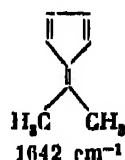


Table II-86 1600 cm^{-1} region of the $\nu\text{C}=\text{C}$ vibration in fulvenes

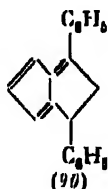
Fulvene has a medium intensity band at 1664 cm^{-1} [183]. On substitution of the hydrogen atoms with methyl or alkyl groups the band is slightly shifted towards lower frequencies. Methyl- and dimethylfulvenes have strong absorptions at 1645 and 1642 cm^{-1} , respectively. Phenyl groups on the exocyclic carbon atom lower the frequency considerably. Methylphenylfulvene absorbs at 1626 cm^{-1} , furylfulvene [184] at 1629 cm^{-1} , and diphenylfulvene at 1597 cm^{-1} . The decrease in frequency is followed by an appreciable decrease in intensity.

Condensation with an aromatic ring (benzofulvenes) does not affect the frequency very much. Dimethylbenzofulvene absorbs at 1637 cm^{-1} ; and methylphenylbenzofulvene, at 1613 cm^{-1} . The bands are of medium intensity. Diphenylbenzofulvene and similar compounds have weak absorption bands at 1605 and 1504 cm^{-1} which may be assigned to the vibrations of the aromatic ring. Generally, when in fulvenes the characteristic band is absent or very weak, one can assume that the molecule is nonplanar because of steric reasons [184]. In condensed systems like diphenyldihydropentalene (90), the charac-

teristic absorption occurs at 1615 cm^{-1} because of the presence of phenyl groups [185].

The characteristic band of the fulvenic system at 1600 cm^{-1} is better explained by a vibrational coupling involving cross conjugated double bonds [formula (88)] rather than by the vibration of an aromatic type ring in formula (89). This interpretation is in agreement with the physico-chemical properties of fulvenes. The contribution of the exocyclic double bond can be seen from the fact that the spectra of isopropylcyclopentadiene and isopropylindene (obtained by hydrogenation of dimethylfulvene and dimethylbenzofulvene, respectively) do not show the strong absorption at 1640 cm^{-1} , while the 1600 cm^{-1} band arising from the aromatic ring maintains its position and intensity.

2. *The 1300 cm^{-1} region.* Fulvenes have a strong band at $1340\text{--}1370\text{ cm}^{-1}$, readily distinguishable from the symmetrical deformation mode of the CH_3 group. The band occurs in cyclopentadiene and indene at the same frequency and seems to be characteristic for the unsaturated five-membered ring. Fulvene has a strong absorption at 1334 cm^{-1} and diphenyldihydropentalene (90), at 1355 cm^{-1} [185]. In benzofulvenes the band is of medium intensity.

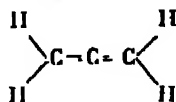


3. *The out-of-plane deformation vibration.* The four hydrogen atoms of the fulvene ring give rise to a strong absorption at 762 cm^{-1} , comparable to the out-of-plane deformation of the four hydrogen atoms in ortho-disubstituted benzenes (see page 207). In fulvene the band arises at 765 cm^{-1} . Benzofulvenes substituted at the exocyclic carbon atom have medium intensity bands at ca. 795 cm^{-1} , benzofulvene at 792 cm^{-1} , dimethylbenzofulvene at 790 cm^{-1} , diphenylbenzofulvene at 797 cm^{-1} , and furylbenzofulvene at 799 cm^{-1} .

d. *Hydrocarbons with cumulated double bonds (allenes)*

The most characteristic absorption in spectra of allenes is due to the symmetrical and asymmetrical vibrations of the $\text{C}=\text{C}=\text{C}$ group.

Allene, the first member of the series has three carbon atoms in a linear arrangement with the CH_2 groups in two planes perpendicular to each other. The symmetry of the molecule is V_d [186, 187].



The symmetrical vibration of the $\text{C}=\text{C}=\text{C}$ bond is inactive in the infrared. The asymmetrical vibration gives rise to a strong absorption at 1980 cm^{-1} .

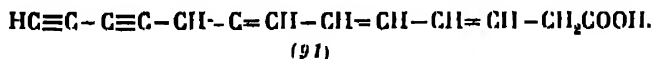
In asymmetrically substituted allenes, both modes are active in the infrared. The symmetrical stretching vibration occurs at 1070 cm^{-1} , and the asymmetrical one, at $1950\text{--}1965\text{ cm}^{-1}$ [188, 189]. In 1,2-butadiene the two bands occur at 1970 and 1064 cm^{-1} [190]; 1,2-heptadiene absorbs at 1950 cm^{-1} [191].

In compounds where conjugation with a carboxyl group is possible, the frequency falls to 1940 cm^{-1} . The band is generally split into two strong components with frequencies at 1930 and 1950 cm^{-1} [191] (Table II-37).

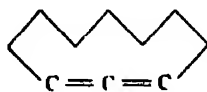
Table II-37 Characteristic frequencies in allenes, cm^{-1}

| $\begin{array}{c} R_1 \\ \diagdown \\ C \\ \diagup \\ X \end{array} = C = C \begin{array}{c} R_2 \\ \diagup \\ C \\ \diagdown \\ R_3 \end{array}$ | | | | |
|---|----------|-------|-------|-------------|
| R_1 | X | R_2 | R_3 | $\nu C=C=C$ |
| C_6H_5 | H | H | H | 1940 |
| H | COOH | H | H | 1930 1950 |
| C_6H_5 | (NH_2) | H | H | 1930 1950 |

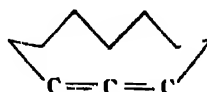
In conjugated straight chains, the frequency falls to 1930 cm^{-1} and in some cases to 1900 cm^{-1} [188]. In the complex molecule of the antibiotic micomycin (91), the allenic bond was identified by the strong band at 1930 cm^{-1} [192, 193]:



The presence of cumulated double bonds in cyclic nine- and ten-membered ring compounds has been shown by the strong band at 1960 cm^{-1} in the infrared spectrum of cyclononadiene-1, 2 (92) and cyclodecadiene-1, 2 (93) [191].



(92)



(93)

Tetraphenylallene and other symmetrical allenes do not absorb in this region [193, 195]. They are characterized by bands arising from the aromatic rings.

4. Unsaturated hydrocarbons with triple bonds (alkynes or acetylenes)

The sp hybridization of the triple-bonded carbon atoms increases the force constant of the $C\equiv C$ and $C-H$ bonds in acetylenes. This results in a considerable increase in frequency of the $\nu C\equiv C$ and $\nu C-H$ vibrations which can

be readily identified in the 2100–2300 cm^{-1} and 3300–3400 cm^{-1} regions.

As in the case of alkenes, the infrared spectra of hydrocarbons in the alkyne series are described on the basis of the vibrational analysis of the first member.

a. Acetylene

The linear, centrosymmetric acetylene molecule ($D_{\infty h}$) symmetry; (Fig. II-41) has seven fundamental vibration modes; three correspond to the stretching vibrations of $\text{C}\equiv\text{C}$ and $\text{C}-\text{H}$ bonds, and the remaining four (degenerate) correspond to the deformation vibrations $\text{C}\equiv\hat{\text{C}}-\text{H}$ [196, 197] (Table II-38).

The existence of a center of symmetry in the acetylene molecule, supported by the validity of the mutual exclusion rule of infrared and Raman spectra, predicts three possible structures (Fig. II-41.)

The model with C_{2h} symmetry should have three vibrations of the A_g type, one vibration of the A_u type, and two vibrations of the B_u type (see Table I-11).

The model with V_h symmetry should have two vibrations, A_g , and one vibration each of the types B_{1g} , B_{1u} , B_{2u} , and B_{3u} . In both cases three out of six fundamental vibration modes should be active in Raman and three in the infrared. Indeed, experimentally, three bands are seen in Raman and three in the infrared. However, only two bands in the infrared (729 and

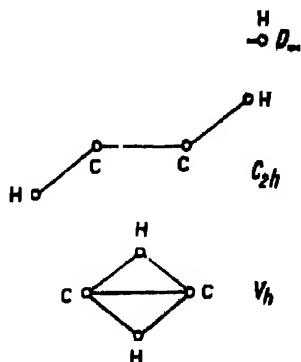


Fig. II-41 The three possible structures of the acetylene molecule.

Table II-38 Frequencies of the fundamental vibrations in acetylene (gas)

| Vibration | Species | Activity | Frequency, cm^{-1} |
|--|--------------|----------|-----------------------------|
| CH stretching sym | Σ_g^+ | R | 3373.7 |
| $\text{C}\equiv\text{C}$ stretching | Σ_g^+ | R | 1973.8 |
| CH stretching asym | Σ_u^+ | IR | 3287 |
| $\text{C}\equiv\hat{\text{C}}-\text{H}$ deformation sym | Π_g | R | 612 |
| $\text{C}\equiv\hat{\text{C}}-\text{H}$ deformation asym | Π_u | IR | 729 |

3287 cm^{-1}) correspond to fundamental vibrations. The third band (1328 cm^{-1}) is obviously a combination band $\nu_4 + \nu_5$. Such a partition is possible only in the case of a linear molecule (Fig. II-41).

The analysis of rotational-vibrational bands in the spectrum of acetylene fully supports the linear centro-symmetric structure.

Monodeuteroacetylene C_2HD does not have a center of symmetry. All the bands present in the infrared also occur in the Raman spectrum [196] (Table II-39).

Table II-39 Fundamental frequencies (cm^{-1}) in acetylene and deuterioacetylene

| Assignment | C_2H_2 | | C_2HD | | C_2D_2 | |
|------------|----------|------|---------|------|----------|---------|
| | IR | R | IR | R | IR | R |
| ν_1 | | 3374 | 3335 | 3335 | | 2700 |
| ν_2 | 3287 | | 2584 | | 2427 | |
| ν_3 | | 1973 | 1851 | 1851 | | 1762 |
| ν_5 | 729 | | 683 | | 539 | |
| ν_4 | | 612 | 518 | | | (505) * |

* Calculated value.

b. Substituted acetylenes

Degree of substitution and molecular symmetry play an important role in the identification of the triple bond.

Monosubstituted acetylenes have a terminal $\equiv C-H$ bond and can be easily identified by the strong absorption bands of $\equiv C-H$ and $C\equiv C$ linkages.

In disubstituted compounds, the $C\equiv C$ stretching vibration has variable intensity, depending on the position of the triple bond in the chain. The $\equiv C-H$ vibration is absent. In this case, the identification of the triple bond is difficult. However, the presence of a band in the characteristic region strongly favors the acetylenic structure. Some combination bands are also significant. Deformation vibrations are characteristic only in the case of monosubstituted compounds.

a. **$C\equiv C$ stretching vibrations.** In acetylene the $C\equiv C$ stretching vibration gives rise to an absorption at 1974 cm^{-1} in the gas phase and at 1965 cm^{-1} in the liquid phase. In mono- and disubstituted acetylenes the frequency increases, falling in the range $2100-2260\text{ cm}^{-1}$ [198]. Within these limits, the two types of acetylenes have the following frequencies:

1. monosubstituted acetylenes ($RC\equiv CH$), $2100-2140\text{ cm}^{-1}$;
2. disubstituted acetylenes ($RC\equiv CR$), $2100-2260\text{ cm}^{-1}$.

The nature of the substituent has a certain influence on the frequency.

The characteristic frequencies in hydrocarbons $R-C\equiv CH$, where R-alkyl or aryl, are shown in Table II-40.

In acetylenic compounds $H_2C\equiv CCH_2X$, where X is a polar group or an electronegative atom, a number of satellite bands are present [199, 200] which are assigned to overtones or combinations.

In propargyl halides ($XCH_2C\equiv CH$), the frequency is slightly higher than in hydrocarbons (Table II-41).

Table II-40 Characteristic frequencies (cm^{-1}) in compounds with a terminal acetylenic group [199]

| Hydrocarbon | Stretching vibration | | Deformation | | Deformation overtones |
|---|----------------------|-----------------------------|------------------------------|-----------------------------------|------------------------------------|
| | νCH | $\nu\text{C}\equiv\text{C}$ | $\nu\text{C}-\text{C}\equiv$ | $\text{C}\equiv\text{C}-\text{H}$ | $-\text{C}\equiv\text{C}-\text{H}$ |
| $\text{HC}\equiv\text{CCH}_3$ | 3320 3300* | 2130 | 930 | 630 | 1249 |
| $\text{HC}\equiv\text{CCH}_2\text{R}$ | 3320 3290* | 2121 | 924-959 | 628-633 | 1242-1249 |
| $\text{HC}\equiv\text{CC}_6\text{H}_5$ (vapor) | 3340 3320* | 2120 | — | 613-642 | 1219 |
| $\text{HC}\equiv\text{CC}_6\text{H}_5$ (solution) | 3316 3305* | 2115 | — | 611-648 | 1219 |

* Shoulder

Table II-41 Characteristic frequencies (cm^{-1}) in $\text{XCH}_2\text{C}\equiv\text{CH}$ [199]

| | νCH | | $\nu\text{C}-\text{C}$ | |
|--|----------------|----------------------|------------------------|----------------------|
| | Main band | Satellite (shoulder) | Main band | Satellite (shoulder) |
| $\text{HC}\equiv\text{CCH}_2\text{I}$ | 3315 | 3298 | 2128 | 2109, 2148 |
| $\text{HC}\equiv\text{CCH}_2\text{Br}$ | 3315 | 3300 | 2126 | 2121 |
| $\text{HC}\equiv\text{CCH}_2\text{Cl}$ | 3315 | 3299 | 2131 | 2126 |
| $\text{HC}\equiv\text{CCH}_2\text{F}$ | 3322 | 3310 | 2148 | — |
| $\text{HC}\equiv\text{CCH}_2\text{OH}$ | 3316 | 3296 | 2120 | — |
| $\text{HC}\equiv\text{CCH}_2\text{OCCH}_3$ | 3317 | 3296 | 2119 | 2104 |
| $\text{HC}\equiv\text{CCH}_2\text{NR}_2$ | 3311-3316 | 3295-3303 | ca. 2110 | — |

Table II-42 $\nu\text{C}\equiv\text{C}$ frequency (cm^{-1}) in disubstituted acetylenes [198]

| Compound | X-H | X-Cl | X-Br |
|---|------|------|------|
| $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-(\text{CH}_3)_3-\text{X}$ | 2210 | — | 2200 |
| $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-(\text{CH}_3)_3-\text{X}$ | 2190 | 2210 | — |
| $n\text{-C}_6\text{H}_{13}-\text{C}\equiv\text{C}-(\text{CH}_3)_3-\text{X}$ | 2190 | — | 2220 |
| $n\text{-C}_6\text{H}_{13}-\text{C}\equiv\text{C}-\text{CH}_3-\text{X}$ | 2210 | 2240 | 2220 |

In symmetrical disubstituted acetylenes, the $\nu\text{C}\equiv\text{C}$ vibration is forbidden in the infrared. It becomes active in asymmetrical molecules. The frequency of the vibration is higher than in monosubstituted compounds. In alkylacetylenes it lies in the range 2190-2210 cm^{-1} (Table II-42) [198, 201, 202].

Several isolated triple bonds increase the number of bands in the 2000 cm^{-1} region [198, 203, 204]. Tridecatriyne-5, 8 has three bands, 2262, 2227, and

2188 cm^{-1} [203]. In nonadiyne-1, 4 the absorption bands have the following frequencies: 2299, 2242, and 2132 cm^{-1} [204].

In cycloalkynes with 8–10 carbon atoms, $\text{C}\equiv\text{C}$ absorptions occur at 2202–2207 cm^{-1} .

Cyclooctyne absorbs at 2208 cm^{-1} [205], cyclononyne and cyclodecyne at 2203 cm^{-1} [206]. A decrease by 40–50 cm^{-1} is observed cf. acyclic compounds (octyne-5 and decyne-5 absorb at 2250 cm^{-1}) [202].

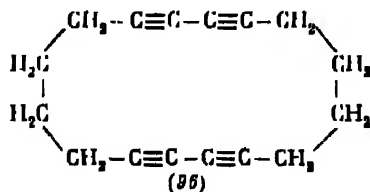
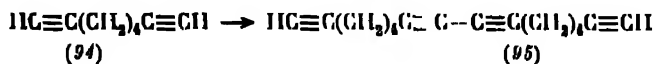
As mentioned above, band intensity varies with the position of the triple bond in the chain. The highest intensity is observed in the terminal triple bond and decreases progressively when the triple bond shifts towards the center of the chain. This is believed to be due to the increase in molecular pseudo-symmetry [197]. For this reason the absence of the $\nu\text{C}\equiv\text{C}$ band is not definitive proof for the absence of a triple bond.

In compounds where the triple bond is conjugated with a double bond or with a benzene ring, a small decrease in frequency is observed [197, 199, 201]. However, the decrease in frequency is much smaller than in the case of conjugated alkenes. In phenylacetylene the frequency falls to 2115 cm^{-1} , (only by 6 cm^{-1}), cf. 2121 cm^{-1} in alkylacetylenes $\text{RCH}_2\text{C}\equiv\text{CH}$.

In conjugated polyyne with at least three $\text{C}\equiv\text{C}$ groups, the increase in frequency is large enough to enable identification [207]. $\text{CH}_3(\text{C}\equiv\text{C})_3\text{CH}_3$ has a weak band at 2222 cm^{-1} . In $\text{CH}_3(\text{C}\equiv\text{C})_4\text{CH}_3$ a medium intensity band occurs at 2237 cm^{-1} [207].

In molecules with various types of triple bonds, the terminal one can be differentiated from the others. A classical example is the spectrum of the complex molecule, mycomycin (see page 194) [208], which shows two bands in the region of $\nu\text{C}\equiv\text{C}$ vibrations. The band at 2040 cm^{-1} was assigned to the terminal triple bond and that at 2200 cm^{-1} to the internal triple bond.

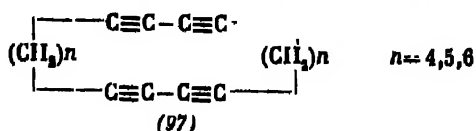
Hexadecatetrayne-1, 7, 9, 15 (95), the dimer of octadiyne-1, 7 (94) [209] has three bands in the $\nu\text{C}\equiv\text{C}$ region; 2235, 2135, and 2102 cm^{-1} . The first two were assigned to vibrations of the disubstituted acetylene and the third one to the terminal $\text{C}\equiv\text{C}-\text{H}$ group [209].



The cyclic dimer of octadiyne-1, 7-cyclohexadecatetrayne-1, 3, 9, 11 (96), containing two linear parallel chains of diacetylene absorbs at 2210 and 2154 cm^{-1} [209, 210].

Some macrocyclic polyyne with $\text{C}\equiv\text{C}-\text{C}\equiv\text{C}$ groups show a doublet at 2247 and 2151 cm^{-1} [210].

A series of macrocyclic polyynes with the general formula (97) show the frequencies of the $\text{—C}\equiv\text{C—C}\equiv\text{C—}$ group at 2239 and 2138 cm^{-1} [211].



b. $\equiv\text{C—H}$ stretching vibration. Since acetylene has a center of symmetry, only the asymmetrical $\equiv\text{C—H}$ vibration is active in the infrared. It occurs at 3287 cm^{-1} . In acetylenic hydrocarbons in the vapor phase, the strong band in the range 3300–3380 cm^{-1} was assigned to this vibration [197].

The position and high intensity of this band enables the identification of this linkage. It can be distinguished from the CII linkage in alkenes, aromatic compounds, or from OH and NH groups.

The frequency of this vibration is constant in position and not affected by structural changes in the rest of the molecule. Tables II-40 and II-41 show that almost all monosubstituted acetylenes have about the same frequencies under identical experimental conditions.

In carbon tetrachloride solution, the frequencies lie in the range 3310–3320 cm^{-1} [199]. The constant position of the $\equiv\text{CH}$ vibration frequency is explained by the fact that the C—H bond is isolated from the rest of the molecule by $\text{C}\equiv\text{C}$ groups and is not affected by the R group in $\text{RC}\equiv\text{CH}$. However, the frequency is very sensitive to variations in physical state [197, 199]. Methylacetylene in the gaseous state absorbs at 3380 cm^{-1} and in the liquid state, at 3305 cm^{-1} [197].

The highest absorption in phenylacetylene occurs at 3340 cm^{-1} in the vapor phase, at 3316 in carbon tetrachloride solution, and at 3329 cm^{-1} in cyclohexane solution [199]. *p*-Nitrophenylpropargyl ether ($\text{O}_2\text{N—C}_6\text{H}_4\text{O—CH}_2\text{C}\equiv\text{CH}$) absorbs at 3313 cm^{-1} in carbon tetrachloride solution and at 3267 cm^{-1} in the solid state. This behavior was explained by the participation of the CII linkage in hydrogen bonding which was observed in several other instances as well [212]. On hydrogen bonding with donor molecules (ethers, amines), the νCH band shifts by 20–40 cm^{-1} towards lower frequencies [213, 211]. A weak band occurring as a shoulder on the main band of the νCH vibration was assigned to a combination between the first overtone of the $\equiv\text{CH}$ deformation mode at 1250 cm^{-1} and the fundamental $\nu\text{C}\equiv\text{C}$ vibration at 2120 cm^{-1} . The relatively high intensity of the band is probably due to a Fermi resonance with the C—H fundamental [199].

c. $\equiv\text{C—H}$ deformation vibrations. All acetylenic compounds of the type $\text{R—C}\equiv\text{CH}$ have one or two strong bands in the 610–680 cm^{-1} region [197, 199]. The absorption was assigned to a deformation of the $\equiv\text{C—H}$ band [197]. In molecules with a three-fold or ∞ -fold axis the two C—H deformation modes are degenerate and a single band occurs in the spectrum. In methylacetylene (in the vapor phase), the band arises at 633 cm^{-1} [197], and in CS_2 at 630 cm^{-1} [199]. In less symmetrical compounds the two equivalent compo-

nents of this doubly degenerate vibration occur as a more or less distinct doublet. Phenylacetylene in the vapor phase shows two absorption maxima at 642 and 613 cm^{-1} . The 613 cm^{-1} band belongs to type C (strong *Q* branch). It was assigned to the nonplanar $\equiv\text{C}-\text{H}$ deformation. The 642 cm^{-1} band, without the *Q* branch, was assigned to the $\equiv\text{C}-\text{H}$ deformation in the plane of the acetylenic triple bond [199].

The overtone of the $\equiv\text{C}-\text{H}$ deformation vibration has an appreciable intensity in spectra of monosubstituted acetylenes, occurring in the range 1245–1260 cm^{-1} (in methylacetylene, at 1260 cm^{-1}).

d. **Other vibration modes in acetylenes.** All acetylenic compounds have bands in the 900–960 cm^{-1} region assigned to the stretching vibration of the C–C bond adjacent to the triple bond. The spectrum of methylacetylene (vapor) shows a band at 928 cm^{-1} , which slightly shifts its position (to 930 cm^{-1}) in CS_2 solution [197]. Since they occur in a crowded region these bands cannot be correlated with structural details. Skeletal deformations arise in the low frequency region, 300–350 cm^{-1} [199].

C. AROMATIC HYDROCARBONS

Aromatic hydrocarbons have characteristic absorptions in the region of C–H stretching vibrations (3000–3100 cm^{-1}), C–H deformation vibrations (650–900 cm^{-1}), and C–C stretching vibrations (1450–1650 cm^{-1}). Characteristic overtone and combination bands of lower intensity occur in the range 1660–2000 cm^{-1} . Along with bands arising in the deformation mode region they enable us to assess the degree and type of substitution of the benzene ring. Although in some regions absorptions of aromatic hydrocarbons overlap with those of alkenes, the presence of an aromatic ring can be established readily by taking into account the position and intensity of bands in all the regions mentioned above.

1. Monocyclic aromatic hydrocarbons

a. **Benzene.** Benzene is one of the few molecules with a large number of atoms for which a complete vibrational analysis has been carried out. The interpretation of infrared and Raman spectra has contributed much to the elucidation of the structure of the benzene molecule, one of the fundamental problems of organic chemistry. The analysis was possible because of the high degree of symmetry of the molecule. The choice between possible models was made by changing the molecular symmetry by means of selective deuteration and by comparing the Raman and infrared spectra of the deuterated compounds with the corresponding theoretical spectra. The Kekulé structure (98) with D_{6h} symmetry could be excluded by showing that the benzene molecule belongs to the point group D_{6h} (Fig. 11.42), where all C–C bonds are equivalent (98a).



The 20 normal vibrational modes of the C_6H_6 molecule with D_{6h} symmetry are shown in Fig. II-43 [215-217].

Four vibrational modes are active in the infrared (A_{2u} and $3E_{1u}$) and seven in Raman ($2A_{1g}$, $4E_{2g}$ and E_{1g}) (the mutual exclusion rule is applied). The other nine modes are forbidden both in Raman and the infrared.

The infrared spectrum shows five strong bands at 671, 1037, 1485, 3045, and 3099 cm^{-1} (Fig. II-44). The last two are a resonance doublet of the fundamental vibration ν_{18} and the combination $\nu_{18} + \nu_{13}$ (Herzberg notations). A third band observed in the ν_{CII} region at 3073 cm^{-1} arises from the combination $\nu_2 + \nu_{18} + \nu_{18}$, resulting from the resonance of the fundamental ν_{18} with the combination $\nu_2 + \nu_{18}$. Theoretically, these resonances cannot take place in the C_6D_6 molecule. Indeed, the infrared spectrum of hexadeutero-benzene shows a single band in this region at 2294 cm^{-1} (Fig. II-44). This fact strongly supports the D_{6h} symmetry [215].

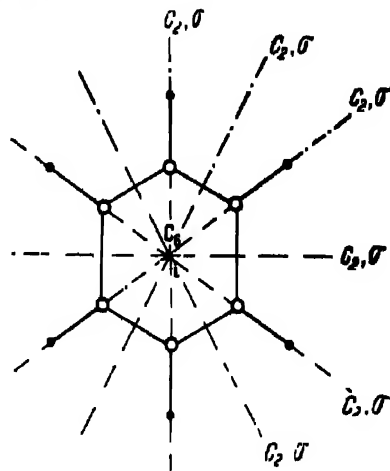


Fig. II 12 D_{6h} symmetry of benzene.
 \circ — carbon atom; \bullet — hydrogen atom; C_2 — axis of symmetry; σ_h — plane of symmetry; i — center of symmetry.

The 671 cm^{-1} band in the spectrum of benzene (503 cm^{-1} in C_6D_6) corresponds to the in-phase periodic vibration of the six hydrogen (or deuterium) atoms in a plane perpendicular to that of the six carbon atoms.

The 1037 cm^{-1} band (813 cm^{-1} in C_6D_6) arises from a deformation vibration of the carbon-hydrogen (deuterium) bonds.

The 1485 cm^{-1} (1333 in C_6D_6) band corresponds to a deformation vibration of the ring.

Only the vibration occurring at 671 cm^{-1} is a true deformation vibration. The other modes (see Fig. II-43) involve motions along the C—H valence lines. In these cases a differentiation between stretching and deformation modes is no longer possible [217-219].

Substitution of one or several hydrogen atoms in the benzene molecule results in loss of the D_{6h} symmetry and a corresponding increase in infrared active vibrations. Monosubstituted compounds C_6H_5X where X is monoatomic, belong to the point group C_{2v} [220]. Even if X is polyatomic, the local symmetry of the ring is preserved so that the characteristic vibrations maintain their symmetry type. In molecules with C_{2v} symmetry, the normal vibration modes are divided into four species (symmetry classes; see page 80): $A_1(\pi)$, $A_2(\gamma, s)$, $B_1(\sigma)$, and $B_2(\gamma, as)$. All vibrations except those of the A_2 type are

| | | | |
|---|---|---|---|
| ν_1 (ν_2) A_{1g} ν_{CC} 392 (R) | ν_2 (ν_1) A_{1g} ν_{CH} 3062 (R) | ν_3 (ν_3) A_{2g} β_{CH} 1326 (IR) | ν_4 (ν_9) B_{2g} τ_{CC} 703 (IR) |
| ν_5 (ν_7) B_{2g} τ_{CH} 985 (IR) | ν_6 (ν_{10}) E_{2g} β_{CC} 606 (R) | ν_7 (ν_{13}) E_{2g} ν_{CH} 3047 (R) | ν_8 (ν_{16}) E_{2g} ν_{CC} 1585 (R) |
| ν_9 (ν_{17}) E_{2g} β_{CH} 1176 (R) | ν_{10} (ν_{11}) E_{1g} τ_{CH} 850 (R) | ν_{11} (ν_6) A_{2u} τ_{CH} 571 (IR) | ν_{12} (ν_8) B_{1u} β_{CC} 1010 (IR) |
| ν_{13} (ν_5) B_{1u} ν_{CH} 3060 (IR) | ν_{14} (ν_1) B_{2u} ν_{CC} (IR) | ν_{15} (ν_{10}) B_{2u} β_{CH} 1110 (IR) | ν_{16} (ν_{20}) E_{2u} τ_{CC} 405 (IR) |
| ν_{17} (ν_{19}) E_{2u} τ_{CH} 970 | ν_{18} (ν_{14}) E_{1u} β_{CH} 1037 (IR) | ν_{19} (ν_{13}) E_{1u} ν_{CC} 1480 (IR) | ν_{20} (ν_{12}) F_{1u} ν_{CH} 3080 (IR) |

Fig. 11-43 Vibration modes of the benzene molecule. In each square are shown: Wilson notation (ν_1 – ν_{20}) [216], Herzberg notation (in brackets) [215], species ($2A_{1g}$, $1A_{2g}$, $4B_{2g}$, $4E_{2g}$, $1E_{1g}$, $1A_{2u}$, $2B_{1u}$, $2B_{2u}$, $2E_{2u}$, and $3E_{1u}$), and vibration type (ν_{CC} , ν_{CH} , β_{CC} , β_{CH} , τ_{CC} , τ_{CH}). Under the scheme of each vibration mode, frequency and activity in Raman or the infrared are shown (R = active in Raman, IR = active in the infrared, I = inactive). The arrows show the displacements of nuclei in the plane of the molecule; +, displacements above the plane; –, displacements below the plane. For each degenerate mode, only one of the three component vibrations is shown.

allowed in the infrared. The vibration modes of the C_6H_5-X molecule are shown schematically in Fig. II-45. All C—H stretching vibrations occur at frequencies in the range $3000-3100\text{ cm}^{-1}$. Theoretically the number of νCH fundamentals should be equal to the number of hydrogen atoms attached

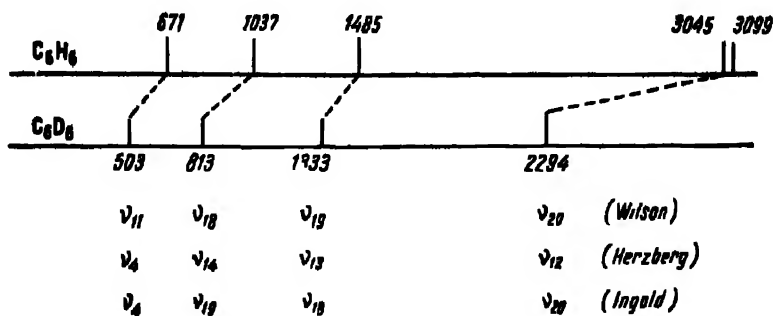


Fig. II-44 Infrared active fundamental frequencies in C_6H_6 and C_6D_6 .

to the ring. In the majority of cases the assignment of bands in this region is extremely difficult. The five νCH vibrations of monosubstituted compounds are not shown in Fig. II-15.

b. **C—H stretching vibrations.** Absorption bands of C—H stretching modes in aromatic hydrocarbons occur at $3000-3100\text{ cm}^{-1}$. Thus aromatic hydrocarbons differ from saturated hydrocarbons which absorb below 3000 cm^{-1} (except small ring compounds). As shown, benzene has three bands in this region; only the band at 3080 cm^{-1} is the fundamental.

In spectra of substituted derivatives, two to five bands occur in the $3000-3100$ region, depending on the number and position of substituents [221, 222]. Only the strongest band is considered fundamental. The other bands correspond to combinations of vibrations in the $1400-1600\text{ cm}^{-1}$ [222]. In the majority of monosubstituted derivatives of benzene C_6H_5X ($X = \text{Hal, alkyl, NH}_2, \text{OCH}_3, \text{CHO, etc.}$), the bands are grouped in the ranges $3027-3039\text{ cm}^{-1}$, $3053-3078\text{ cm}^{-1}$, and $3084-3096\text{ cm}^{-1}$ [222]. In many instances it was observed that the number of these bands decreases with increasing number of substituents, but this is not a general rule.

Table II-43 shows absorptions in the $3000-3100\text{ cm}^{-1}$ in spectra of some alkylbenzenes. Changes in the aggregation state of the sample do not result in shifts greater than 10 cm^{-1} .

c. **C—H Out-of-plane deformation vibrations.** ($\gamma\text{C—H}$). In benzene the in-phase deformation vibration of the six hydrogen atoms perpendicular to the plane of the ring occurs at 671 cm^{-1} [215]. The corresponding absorption band is very strong and is one of the four fundamental vibrations active in the infrared.

In substituted derivatives of benzene, deformation vibrations of the remaining ring hydrogen atoms give rise to a strong band in the range $680-1000\text{ cm}^{-1}$. This band has been studied in many aromatic compounds, both

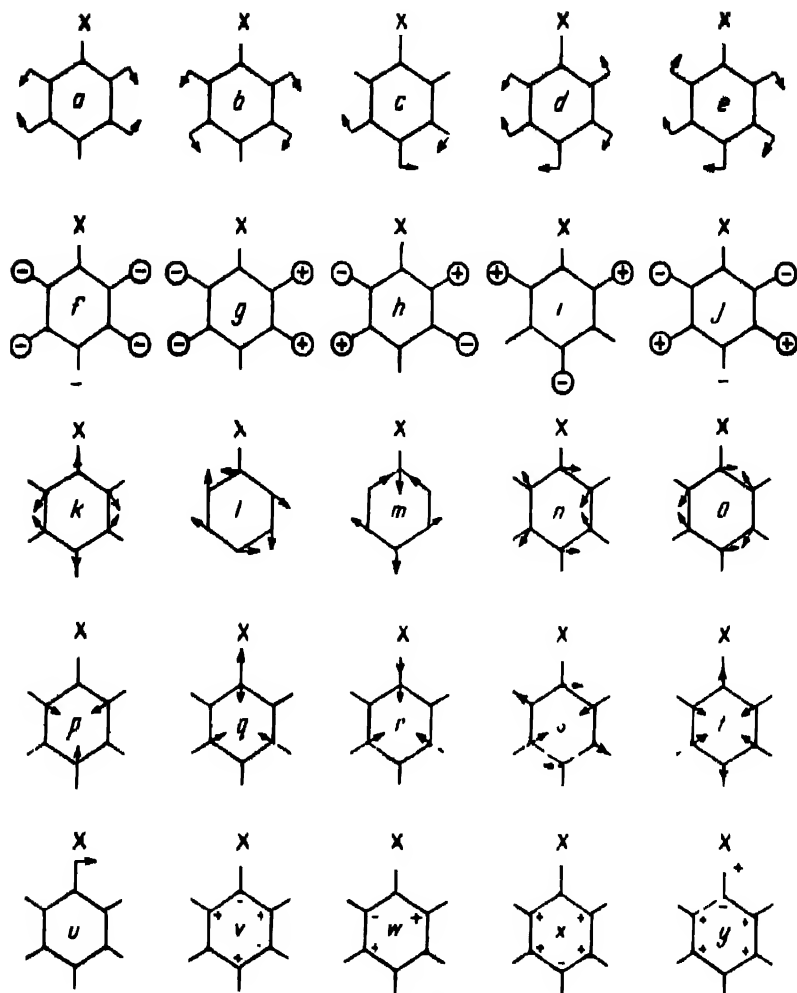


Fig. 11-45 Normal vibration modes of the molecule of monosubstituted benzene (point group C_{2v}) according to D. H. Whiffen [220].

Table 11-11 ν_{CH} Frequencies in alkylbenzenes, cm^{-1}

| Hydrocarbon | ν_{CH} | | | Hydrocarbon | ν_{CH} | |
|---------------------------|------------|------|------|------------------------|------------|------|
| Benzene | 3033 | 3071 | 3091 | <i>p</i> -Xylene | 3013 | 3085 |
| Toluene | 3031 | 3066 | 3088 | 1,3,5-Trimethylbenzene | 3020 | |
| Ethylbenzene | 3028 | 3066 | | 1,2,3-Trimethylbenzene | 3020 | |
| <i>n</i> -Butylbenzene | 3031 | 3066 | 3088 | 1,2,4-Trimethylbenzene | 3003 | 3040 |
| <i>tert</i> -Butylbenzene | 3029 | 3064 | 3091 | | | |
| <i>o</i> -Xylene | 3013 | 3018 | | | | |
| <i>m</i> -Xylene | 3013 | | | | | |

from a theoretical and empirical point of view [200, 223–226]. The frequency of this band depends primarily on the *number and position of substituents* and is practically independent of the nature of substituents [220]. Because of this fact, the $\gamma\text{C}-\text{H}$ band is of great analytical value and is widely used to determine the mode of substitution in the benzene ring. It should be pointed out, however, that in polysubstituted compounds, the intensity of the band decreases sharply, limiting the possibilities of characterization of the mode and degree of substitution. The very strong characteristic bands in alkylbenzenes are of great value in quantitative analysis [225, 227]. These compounds often show two or several strong bands in the $680-900\text{ cm}^{-1}$ region. The second band (which in more complex molecules may be accompanied by weaker bands) arises from other out-of-plane CH deformation modes which become active in the infrared as a result of changes in the molecular symmetry.

Depending on the number of hydrogen atoms on the substituted benzene ring, the spectra show strong bands in the following regions [228, 229, 230];

| | | |
|-------------|--------------------------|----------------------------|
| 5 H vicinal | 730–770 cm^{-1} | 690–710 cm^{-1} * |
| 4 H " | 735–770 | |
| 3 H " | 750–810 | |
| 2 H " | 800–860** | |
| 1 H " | 860–900 | |

The limits of occurrence of characteristic frequencies in mono-, di-, tri-, and tetrasubstituted alkylbenzenes are shown schematically in Fig. II-16 [221, 225, 229].

1. *Monosubstituted benzenes.* In these compounds five hydrogen atoms are attached to the ring. The in-phase deformation vibration of these atoms, which can be visualized as the motion of an opening and closing umbrella, gives rise to a strong absorption in the range $730-770\text{ cm}^{-1}$. The band is readily recognizable because of its very high intensity [229]. It is accompanied by a second, weaker absorption at $694 \pm 11\text{ cm}^{-1}$, assigned to ring deformation and labeled ΦCC [220].

Figure II-17 shows the $667-900\text{ cm}^{-1}$ region in spectra of some alkylbenzenes.

The positions of the $\gamma\text{C}-\text{H}$ band in a number of monosubstituted benzenes are shown in Table II-14 [224].

However, the region assigned to the $\gamma\text{C}-\text{H}$ vibration in monosubstituted compounds overlaps with the characteristic region of γCH vibrations arising from the four hydrogen atoms in ortho-disubstituted compounds. The two classes of compounds can be differentiated by the $700 \pm 10\text{ cm}^{-1}$ band occur-

* Occurs also in 1,3-, 1,3,5-, and 1,2,3-substituted compounds.

** Often at $800-820\text{ cm}^{-1}$.

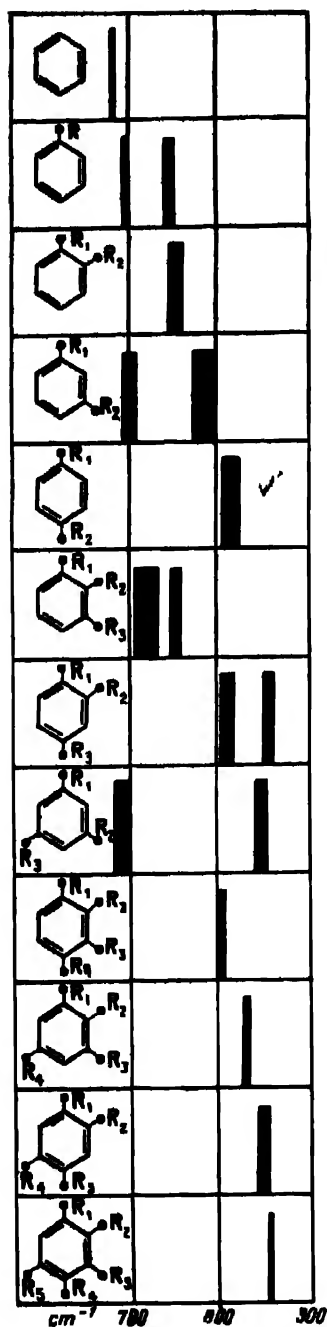


Fig. II-46 Infrared absorptions of some monocyclic aromatic hydrocarbons in the out-of-plane CH deformation mode region.

Table II-47 γ_{CH} Frequencies in monosubstituted benzenes, cm^{-1}

| $\text{C}_6\text{H}_5\text{R}$ | | $\text{C}_6\text{H}_4\text{X}$ | |
|-------------------------------------|---------------|--------------------------------|---------------|
| R | γ_{CH} | X | γ_{CH} |
| CH_3 | 730 | Cl | 742 |
| CH_2CH_3 | 745 | Br | 740 |
| $\text{CH}_2\text{CH}_2\text{CH}_3$ | 740 | NH_2 | 753 |
| $\text{CH}(\text{CH}_3)_2$ | 761 | OCH_3 | 753 |
| $\text{C}(\text{CH}_3)_3$ | 762 | OH | 751 |
| C_6H_5 | 752 | | |
| $\text{CH}_2\text{C}_6\text{H}_5$ | 735 | | |

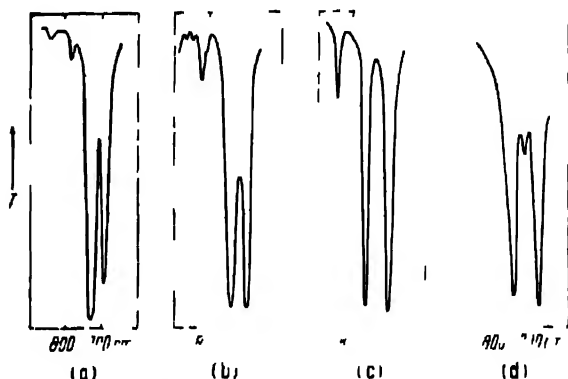


Fig. II-47 Infrared spectra of some monoalkylbenzenes in the C-H deformation mode region.

(a) Toluene; (b) *n*-butylbenzene; (c) *tert*-butylbenzene
(d) 2-phenylheptane.

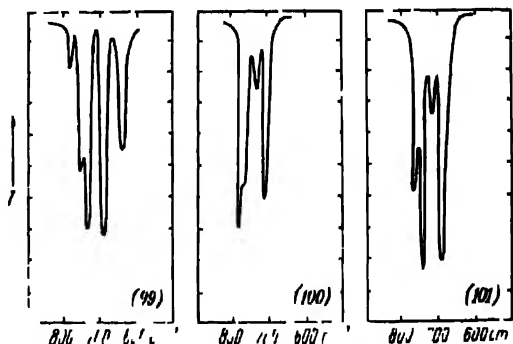
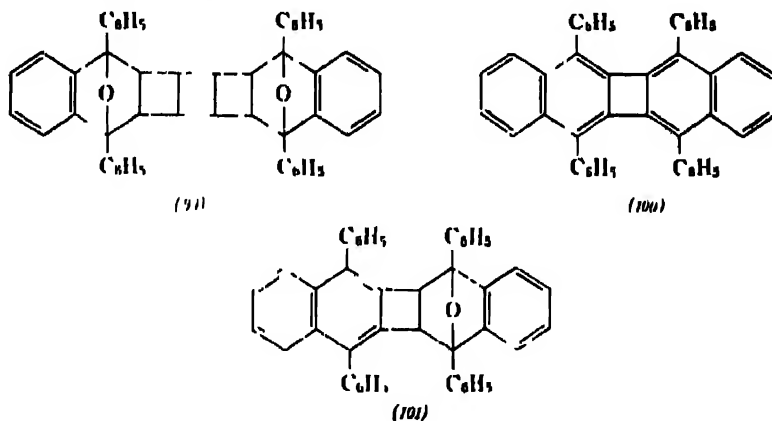


Fig. II-48 Characteristic frequencies of monosubstituted benzenes in polycyclic systems.

ring in monosubstituted derivatives [220]. *ortho*-Disubstituted compounds have a single band in this region (see Fig. II-46). If this band is absent, the presence of a monosubstituted benzene ring cannot be assessed with certainty.

On the other hand, *meta*-disubstituted compounds and 1,3,5-tri-substituted compounds also absorb in the $700 \pm 10 \text{ cm}^{-1}$ region (see Fig. II-46). Consequently this band can give an indication concerning the mode of substitution only if all the characteristic regions of the spectrum are studied (see page 200).

The $700 \pm 10 \text{ cm}^{-1}$ is constant in position even in compounds with complicated structure. The adduct of diphenyl-benzofurane with *anti*-tricyclooctadiene (99), 1,4,5,8-tetraphenyldibenzobiphenylene-2,3,6,7 (100), and its *endoxo* derivative (101) have a strong absorption at $698\text{--}700 \text{ cm}^{-1}$ (Fig. II-48) [230, 231]. The presence of this band confirms the existence of monosubstituted benzene rings. The complicated pattern in the $730\text{--}770 \text{ cm}^{-1}$ region is due to overlap of bands arising both from monosubstituted and *ortho*-disubstituted rings.



In a number of compounds with monosubstituted benzene rings attached to a $\text{C}=\text{C}$, $\text{C}=\text{N}$, $\text{N}=\text{N}$ double bond, it was observed that spectra of *cis* isomers have a larger number of bands than those of *trans* isomers in the $680\text{--}800 \text{ cm}^{-1}$ region; for example, *trans*-azobenzene absorbs at 689 and 776 cm^{-1} (typical pattern for a monosubstituted benzene ring), while *cis*-azobenzene absorbs at 688 , 700 , 756 , and 774 cm^{-1} . Similar behavior is observed in stereoisomers of stilbene, azoxybenzene, benzaldoxime, and the benzene diazotate ion. The phenomenon was attributed to a vibrational perturbation due to steric hindrance of CH bonds in the *ortho* positions [232].

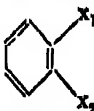
2. *Disubstituted benzenes*. Frequencies of bands assigned to the deformation vibrations of the remaining four $\text{C}-\text{H}$ bonds in the disubstituted benzene ring depend on the position of these bonds in the molecule and are of value in establishing the relative positions of the two substituents.

In alkylbenzenes only *meta*-disubstituted derivatives have two bands: $690\text{--}710 \text{ cm}^{-1}$ and $770\text{--}800 \text{ cm}^{-1}$. The first band occurs in the same region as that characteristic for monosubstituted compounds (see Fig. II-46). *Ortho*-(1,2)-

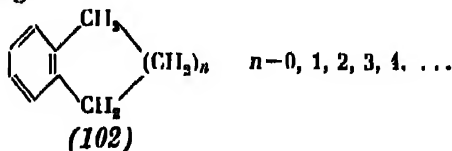
and *para*-(1,4)-disubstituted compounds have a single strong band in this region. In *ortho* derivatives it occurs at 770–760 cm^{-1} and in *para*-derivatives at 810–830 cm^{-1} . In most cases these characteristic absorptions are of value both for establishing the type of substitution and for quantitative analysis.

In the case of identical substituents in the *ortho*-position, it was possible to calculate the frequencies corresponding to the γCH vibration. Only vibration modes belonging to the B_2 class (783–968 cm^{-1}) have strong absorptions in the infrared. In *ortho*- $\text{C}_6\text{H}_4\text{I}_2$ the very strong band at 751 cm^{-1} is assigned to this type of vibration. The band position is independent of the nature of substituents, as in the case of monosubstituent derivatives [220, 224]. In Table II-45 are shown frequencies of some *ortho*-disubstituted benzenes.

Table II-45 γCH frequencies in *ortho*-disubstituted benzenes

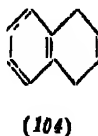
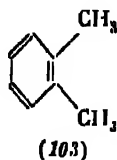
|  | | |
|---|------------------------|-----------------------------------|
| X_1 | X_2 | $\gamma\text{CH}, \text{cm}^{-1}$ |
| CH_3 | CH_3 | 743 |
| C_2H_5 | C_2H_5 | 752 |
| Cl | Cl | 750 |
| CH_3 | NH_2 | 753 |
| CH_3 | OH | 752 |

In spectra of aromatic compounds with the general formula (102), characteristic changes are observed, depending on the size of the cycloalkene ring.

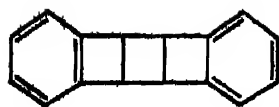


In the case of tetralin (104), a single strong band at 746 cm^{-1} is observed, the same as in *o*-xylene (103), which means that closure of a strain-free ring does not change the νCH vibrations in the benzene ring [233]. The

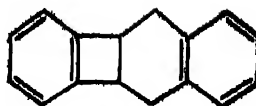
more strained the cycloalkene ring, the more dependent becomes the vibration on the type of substitution. Indane (105) shows two bands, 739 and 752 cm^{-1} . In benzocyclobutene (106) the bands are still further apart: 714 and 781 cm^{-1} [234]. The characteristic frequencies of these fundamental systems are shown in Fig. II-49. 3,1,7,8-Dibenzotricyclo [4.2.0.0^{2,5}] octa-



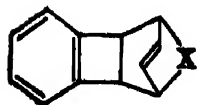
diene-3,7 (107) has three bands, 721, 747, and 773 cm^{-1} . The middle band is very strong [235]. This group of bands is considered characteristic for the benzocyclobutene system (Fig. II-50). The same pattern can be seen in other compounds containing the benzocyclobutene system. In the spectrum of 3,4,7,8-dibenzobicyclo [4.2.0] octadiene-3,7 (108), formed by condensation of *o*-quinodimethane with benzocyclobutadiene, the out-of plane deformation vibration of the hydrogen atoms attached to the benzene ring give rise to a group of bands with frequencies 730, 748 and 765 cm^{-1} [236, 237].



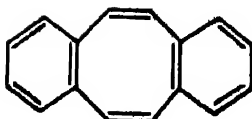
(107)



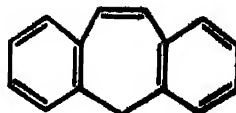
(108)

X-CH₂

(109)



(110)



(111)

In more complicated systems of type (109), the spectra support the above assignments [230].

1, 2, 5, 6 -Dibenzocyclooctatetraene (110) shows bands at 755 and 776 cm^{-1} (Fig. II-51). Dibenzocycloheptatriene (111) shows bands at 729, 739, and 760 cm^{-1} .

Meta-disubstituted compounds have two bands in the γCH region, in the range 680–725 cm^{-1} and 750–810 cm^{-1} [229].

In alkylbenzenes the limits are 690–710 cm^{-1} and 770–800 cm^{-1} [225]. These bands are of limited analytical value because both monosubstituted and 1,2,3-trisubstituted compound absorb in this region.

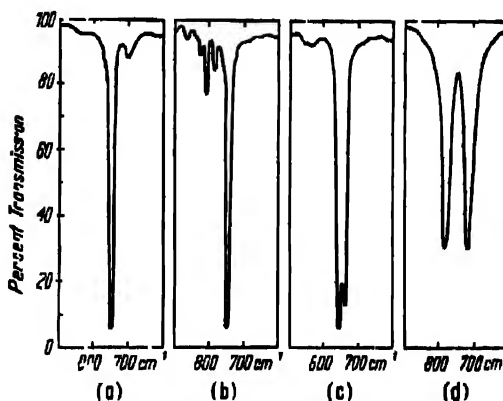


Fig. II-49 Infrared spectrum of *o*-xylene (a), tetralin (b), indane (c) and benzocyclobutene (d) in the CH deformation mode region.

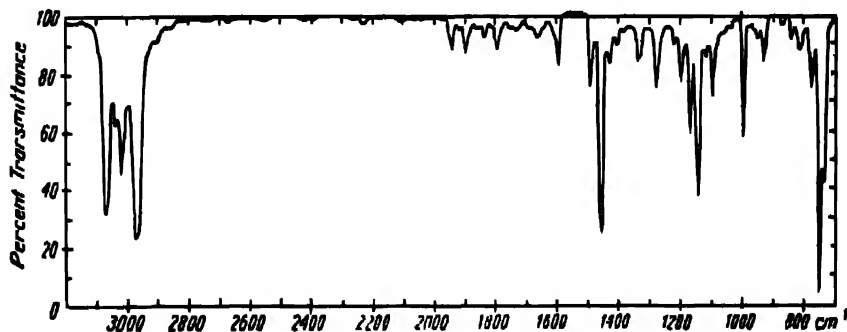


Fig. II-50 Infrared spectrum of 3,4,7,8-dibenzotricyclo[4,2,0,0^{2,5}]octadiene-3,7 (107).

Para-disubstituted compounds have a single band at 800–810 cm^{-1} [220]. Distinction from *meta*-disubstituted compounds is possible since the latter have a second band at lower frequency (see above and Fig. II-46). In order to distinguish *para*-disubstituted benzenes from 1, 2, 3, 4-tetra-substituted ones, the spectra have to be compared in the 1660–2000 cm^{-1} region (see Fig. II-53).

The macrocyclic paracyclophane system (112), in which two benzene rings are linked in *para*-position by bridges of 2–6 methylene groups, shows

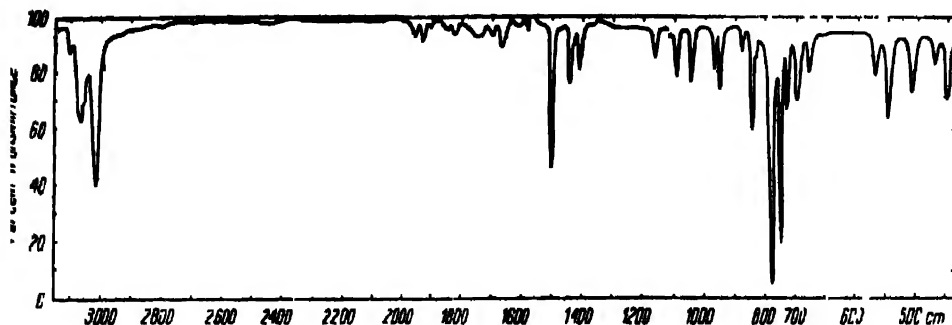
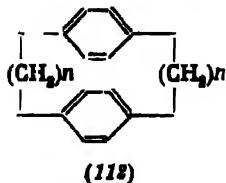


Fig. II-51 Infrared spectrum of 1,2,5,6-dibenzocyclooctatetraene.

anomalies in its infrared and ultraviolet spectra [238]. Table II-46 shows the absorptions in the out-of-plane CH deformation region in compounds with $m=2$ and $n=2,3,4$. The anomalies were interpreted as effects of distortion of the benzene ring and interstitial resonance due to the geometry of the system. The compound with $m=n=2$ has a small distortion of the rings. The molecule with $m=3$ and $n=6$ is planar and has in this region a spectrum analogous to that of acyclic compounds (e.g., 1,4-diethylbenzene or 4,4'-dimethyldibenzyl).

Table II-46 γ CH frequencies
in paracyclophane [238]



| m | n | cm^{-1} | |
|-----|-----|------------------|-----|
| 2 | 2 | 934 | 893 |
| 2 | 3 | 924 | 878 |
| 2 | 4 | 944 | 889 |

3. *Polysubstituted benzenes*. When the number of adjacent hydrogen atoms decreases, the γ CH vibration frequency increases while the band becomes weaker. In penta-substituted compounds, the absorption takes place in the range 870–900 cm^{-1} [239].

All trisubstituted compounds have two strong bands in the 680–900 cm^{-1} region (see Fig. II-46). The lowest γ CH frequency in this series is to be expected in 1, 2, 3-substituted compounds with three adjacent hydrogen atoms. Indeed, all these compounds show strong absorptions at 760–780 cm^{-1} . Their bands may sometimes overlap with those of *meta*-disubstituted compounds, which also have three adjacent hydrogen atoms. The other weaker band occur-

ing at 705–745 cm^{-1} was tentatively assigned to a deformation vibration of the benzene ring (ΦCC) analogous to that of monosubstituted compounds (690–710 cm^{-1}), *meta*-disubstituted compounds (690–710 cm^{-1}), and 1,3,5-trisubstituted compounds (680–700 cm^{-1}). With few exceptions these two bands are of satisfactory analytical value since the γCH frequency is generally above 770 cm^{-1} , while the low frequency band is variable in position and slightly higher than in monosubstituted compounds.


The spectrum of asymmetrically substituted compounds (1,2,4,-) shows both the γCH band of the two adjacent hydrogen atoms (in the 805–825 cm^{-1} region, almost identical to that of *para*-disubstituted compounds) and the band arising from the deformation mode of the isolated hydrogen atom (870–885 cm^{-1}). The band is of medium or, at the most, medium-strong intensity.

1,3,5-Trisubstituted benzenes have a single main band in the region 835–874 cm^{-1} , corresponding to the γCH vibration of the three isolated hydrogen atoms [240]. Obviously the intensity of the band is higher than that of 1,2,4-substituted compounds and the frequency is generally slightly lower.

In identification of symmetrically trisubstituted compounds, the out-of-plane deformation of the aromatic ring (ΦCC) at 680–700 cm^{-1} is of major importance. The infrared spectrum of mesitylene shows a strong band at 835 cm^{-1} , accompanied by a weaker one at 881 cm^{-1} . The absorption at 687 cm^{-1} (ΦCC) enables the identification of symmetrically trisubstituted compounds.

In 1,3,5-trialkylsubstituted compounds, the γCH frequency increases with the number of side chain carbon atoms and with the volume of the alkyl group (Table II-47).

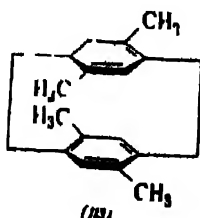
Table II-47 CH frequencies in 1,3,5-trialkylbenzenes (cm^{-1})

$$\text{R}_1 \quad \text{R}_2 \quad \text{R}_3$$


| R_1 | R_2 | R_3 | γCH |
|----------------------------|----------------------------|----------------------------|-------------------|
| CH_3 | CH_3 | CH_3 | 835 |
| CH_3 | CH_3 | C_2H_5 | 845 |
| CH_3 | CH_3 | $(\text{CH}_2)_1\text{CH}$ | 846 |
| CH_3 | CH_3 | $(\text{CH}_2)_2\text{C}$ | 847 |
| C_2H_5 | C_2H_5 | C_2H_5 | 865 |
| CH_3 | $(\text{CH}_2)_1\text{CH}$ | $(\text{CH}_2)_1\text{CH}$ | 857 |
| CH_3 | $(\text{CH}_2)_2\text{C}$ | $(\text{CH}_2)_2\text{C}$ | 858 |
| $(\text{CH}_2)_1\text{CH}$ | $(\text{CH}_2)_1\text{CH}$ | $(\text{CH}_2)_1\text{CH}$ | 870 |
| $(\text{CH}_2)_2\text{C}$ | $(\text{CH}_2)_2\text{C}$ | $(\text{CH}_2)_2\text{C}$ | 874 |

A shift towards higher frequencies is also observed in the distorted benzene rings of the paracyclophane system. The vibration of the isolated

hydrogen atoms on the benzene rings in compound (113) occurs at 906 cm^{-1} [241]. The 710 cm^{-1} band is due to the vibration of the distorted ring. In the analogous unsubstituted compound, the band occurs at 725 cm^{-1} .



Relatively few examples are available for the characterization of tetra- and penta-substituted benzenes. The assignments in the $800\text{--}900\text{ cm}^{-1}$ region, supported to a certain extent by these examples are unreliable.

4. *In-plane CH deformation vibrations* (βCH). Spectra of aromatic compounds show a series of bands of relatively low intensity in the $950\text{--}1225\text{ cm}^{-1}$ region, characterized by their sharp shape. These bands arise mostly from in-plane deformation modes of the ring CH bonds [220]. Their analytical value is diminished both by their low intensity and by the fact that many absorptions occur in this region ($\nu\text{C--C}$, $\nu\text{C--O}$ etc.); however, they may be of value to confirm observations made in other regions.

Existing data show to a certain extent that one can set limits for characteristic absorptions of various substitution modes (see Table II-48).

Table II-48 Groups of bands in the $960\text{--}1225\text{ cm}^{-1}$ region

| Benzenes substituted in positions | Frequency, cm^{-1} |
|-----------------------------------|---------------------------------------|
| 1,2; 1,4; 1,2,4 | 1000–1070* 1090–1125 1175–1225 |
| 1,3; 1,2,3; 1,3,5 | 1000–1070 1070–1110** 1125–1175 |
| 1,2; 1,2,3; 1,2,4 | 960–1000*** |

* Two bands.

** Does not occur in 1,3,5.

*** One band.

The identification of a certain substitution type within each group in Table II-48 is only possible if one considers the absorptions occurring in other characteristic regions of the spectrum.

d. C—C stretching vibrations.

The benzene molecule has three energy levels associated with stretching vibrations of the ring carbon atoms. The first two (E_{1g} , 1585 cm^{-1} and E_{1u} , 1485 cm^{-1}) are doubly degenerate; the third level is not well defined. The only νCC vibration mode active in the infrared (E_{1u}) has a frequency of 1485 cm^{-1} .

By loss of D_{6h} symmetry in substituted compounds, the other C—C stretching modes of the benzene ring also become infrared active. In mono-substituted compounds (point group C_{2v}), the two components of the doubly

absorptions. In some cases the main band has a shoulder; other cases, the absorptions occur separately. The separation of the two levels is much larger in the case of doubly degenerate vibrations occurring at 1485 cm^{-1} (E_{1u}), resulting in the occurrence in the infrared of a strong band at 1499 cm^{-1} (probably due to an A_1 -type vibration) and a second band at 1451 cm^{-1} (component of type B_1).

νCC bands can also be observed in compounds with a higher degree of substitution. Spectra of these compounds show four main absorption bands

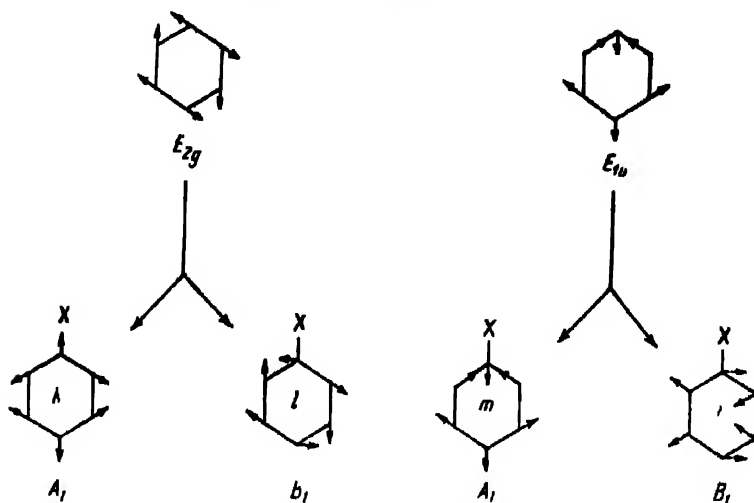


Fig. II-52 Splitting of degenerate modes in going from D_{6h} to C_{2v} symmetry (see also Fig. II-43 and II-45).

in the $1450\text{--}1650\text{ cm}^{-1}$ region, the most characteristic occurring at 1500 and 1600 cm^{-1} [220, 221, 229, 233, 242, 243]. Correlated with bands in the $3000\text{--}3100\text{ cm}^{-1}$ and $680\text{--}900\text{ cm}^{-1}$ regions, they serve for the identification of the aromatic hydrocarbons ring. The absorption at 1500 cm^{-1} differentiates aromatic hydrocarbons from alkenes, which do not have $\nu\text{C}=\text{C}$ bands at such low frequencies. The position of bands in the $1450\text{--}1650\text{ cm}^{-1}$ region in mono- and disubstituted benzenes is shown in Table II-49.

Table II-49 νCC frequencies (cm^{-1}) in mono- and disubstituted benzenes [220]

| Mode of substitution | | | |
|----------------------|--------------------|-----------------|------------------|
| mono | ortho | meta | para |
| $1451 \pm 12s$ | $1445 \pm 8s$ | $1447 \pm 15m$ | $1450 \pm 10m$ |
| $1499 \pm 7vs$ | $1490 \pm 11s$ | $1499 \pm 7vs$ | $1512 \pm 12vs$ |
| $1588 \pm 9w^*$ | $1575 \pm 9^*var$ | $1590 \pm 7s^*$ | $1571 \pm 11w^*$ |
| $1606 \pm 7m^*$ | $1609 \pm 10^*var$ | $1611 \pm 9s^*$ | $1620 \pm 8m^*$ |

* In many compounds these absorptions form a single band. *vs* very strong, *s* strong, *m* medium, *w* weak, *var* variable

Table II-49 shows that in various classes of compounds the bands vary less in position than in intensity. The approximate mean values of frequencies in Table II-49 are 1450, 1500, 1580, and 1610 cm^{-1} . A short description of the four regions containing ν_{CC} bands is given below.

The $1450 \pm 20 \text{ cm}^{-1}$ band. The hypothesis concerning the existence of a ν_{CC} vibration in the 1450 cm^{-1} region [244] was confirmed by an extensive study of a many substituted benzenes [220, 221, 245]. The limits of the region were established from a study of a series of monosubstituted compounds absorbing in the range 1439–1470 cm^{-1} [221]. The band is of little analytical value in the case of alkyl substituted compounds, because of the possibility of overlap with absorptions arising from the CH deformation mode of CH_2 groups. In some instances (nitrobenzene, aniline), the band is of low intensity. The band can be identified readily in halogenated benzene derivatives.

The $1500 \pm 25 \text{ cm}^{-1}$ band. The majority of aromatic compounds have relatively strong absorptions around 1500 cm^{-1} [220, 221, 245]. The bands of *para*-disubstituted and 1,2,4-trisubstituted compounds occur at higher frequencies; 1,2,3-trisubstituted compounds absorb at lower frequencies. The band position seems to be affected by the electronegativity of substituents, but even more so by the relative position of substitution. Consequently, absorptions in this region are not indicative of the nature of substituents, and only in certain instances, in association with the 1600 cm^{-1} band (see below) can they give information with regard to the type of substitution [225].

The $1600 \pm 25 \text{ cm}^{-1}$ and $1580 \pm 20 \text{ cm}^{-1}$ bands. As shown above, in substituted benzenes, the splitting of the doubly degenerate E_{2g} fundamental band is often insufficient for distinct observation of the two components. Their separation is enhanced when the aromatic ring is conjugated with $\text{C}=\text{C}$ [242] or $\text{C}=\text{O}$ [246] double bonds and is accompanied by an appreciable increase in intensity of the 1580 cm^{-1} band. The 1600 cm^{-1} band is very constant in position in monosubstituted compounds ($1600 \pm 7 \text{ cm}^{-1}$). Its frequency decreases in 1,2,3-trisubstituted compounds and increases in *para*-substituted derivatives. In general, shifts of this band in both directions occur simultaneously with those of the 1500 cm^{-1} band. To a certain extent the influence of electronegative substituents results in shifts towards the lower limit [221]. The positions of the 1600 cm^{-1} and 1500 cm^{-1} bands are affected very little by the nature of substituents except for a few compounds where they are shifted towards the extreme limits of the region. In certain instances the relative position of substituents seems to play a more important role in the rather small shift of the band.

Shifts in position of the 1450–1650 cm^{-1} bands are, however, much less important than the observed changes in intensity. In the case of compounds belonging to the point group C_{2v} (*mono*-substituted or *para*-disubstituted derivatives), one may argue about the main reasons leading to variations in band intensity [247].

In the case of substituents which only slightly perturb the charge distribution in the ring, vibrations *c* and *d* (Fig. II-45) should give rise to weak absorptions, while vibrations *e* and *f*, arising from the infrared active fundamental E_{1u} , should share between them the intensity of the corresponding absorption of unsubstituted benzene.

If the nature of the substituent is such that it can alter the charge distribution in the aromatic ring, the change can only be symmetrical with respect to the plane σ_v , perpendicular to the plane of the molecule. Obviously, as far as intensities are concerned, the influence will be felt most strongly by vibrations of type A_1 (Fig. II-45c and e).

However, the relative change in intensity will be larger in *c* and *d* than in *e* and *f* because the very activity of vibrations *c* and *d* depends on the existence of X (and Z in the case of *para*-disubstituted compounds). Consequently, the largest change in intensity associated with perturbation of charge distribution in the aromatic ring is to be expected in the case of the absorption arising from vibration *c* (1600 ± 25 cm⁻¹). The variation is larger for *d* and *e* and relatively small for *f*. The intensity of absorptions arising from vibrations *c* and *d* should increase more or less steadily with increasing charge perturbation. In vibration *e*, the variation cannot be predicted.

For experimental confirmation of these hypotheses, three groups of compounds were chosen, where the substituents are (a) strong electron donors (+E effect; NR₂, OR), (b) weak electron donors (substituents attached to the ring through a saturated carbon atom), and (c) strong electron acceptors (-E effect; C=O, NO₂ directly attached to the ring). Table II-50 shows the mean frequencies and the apparent extinction coefficients of bands in monosubstituted benzenes.

Table II-50 Mean frequencies and apparent extinction coefficients $\epsilon^{(a)}$ in C₆H₅R [247]

| R | Vibration mode | | | | | | | |
|-----------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | $A_1(e)$ | | $B_1(d)$ | | $A_1(e)$ | | $B_1(f)$ | |
| | cm ⁻¹ | $\epsilon^{(a)}$ | cm ⁻¹ | $\epsilon^{(a)}$ | cm ⁻¹ | $\epsilon^{(a)}$ | cm ⁻¹ | $\epsilon^{(a)}$ |
| Strong electron donor | 1603 | 200 | 1586 | 60 | 1498 | 155 | 1451 | 30 |
| Weak electron donor | 1605 | 15 | — | — | 1495 | 40 | 1454 | 45 |
| | (1585)* | 0 | (1585)** | 0 | (1481) | (40) | (1481) | (40) |
| Electron acceptor | 1604 | 50 | 1585 | 35 | 1489 | 15 | 1451 | 55 |

* In benzene a single band at 1585 cm⁻¹ (E_{1g} fundamental, active in Raman) and 1481 cm⁻¹ (E_{1g} , active in the infrared). For clarity the intensity of the E_1 band ($\epsilon^{(a)} = 80$) was equally distributed between the two components.

** Raman frequencies.

As expected, the largest variations were observed in the case of vibration *c* and the smallest is that of vibration *f*. Relative variations in intensity are larger for *c* and *d* than for *e* and *f*. The intensity of the 1500 cm⁻¹ band seems to increase for every electron donating substituent directly attached

to the ring. In nonconjugated systems, the bands in the $1450\text{--}1650\text{ cm}^{-1}$ region are often weak. The 1500 cm^{-1} band is generally stronger. In all compounds where the aromatic ring is conjugated with a double bond ($\text{C}=\text{C}$, $\text{C}=\text{O}$, NO_2 , etc.), band intensities (particularly those in the $1580\text{--}1600\text{ cm}^{-1}$ range, increase. The intensity of the 1500 cm^{-1} band is slightly lower (its intensity falls below that of the $1580\text{--}1600\text{ cm}^{-1}$ bands). In some instances, the 1600 cm^{-1} band becomes so strong that it surpasses that of the carbonyl group. If the latter is involved in hydrogen bonding, the shift of the band cannot be determined with enough accuracy to be of value as a criterion for the degree of association of the molecule.

e. **Ring vibrations.** In the benzene molecule the carbon atoms forming the aromatic ring vibrate as a whole. These vibrations are known as *ring vibrations*. Because of molecular symmetry, all ring vibrations of the benzene molecule are inactive in the infrared. In substituted compounds they give rise to absorptions, some of which are characteristic. Vibration *p* in Fig. II-45, suggesting a "breathing" motion of the ring, is relatively constant in frequency ($1000 \pm 10\text{ cm}^{-1}$) and occurs with variable intensity in monosubstituted, *meta*-disubstituted, and in the majority of trisubstituted compounds completing the characteristic pattern of vibrations in the $900\text{--}1225\text{ cm}^{-1}$ region. Its position is influenced by *ortho*- and *para*-substituents and the absorption cannot be identified. The in-plane deformation mode of the aromatic ring ($\alpha\text{-C-C-C}$) (Fig. II-45 *s*) gives rise to a weak absorption at $620 \pm 4\text{ cm}^{-1}$ in spectra of monosubstituted compounds. One of the most characteristic aromatic bands, which can be identified readily in monosubstituted ($697 \pm 11\text{ cm}^{-1}$), *meta*-disubstituted ($690 \pm 15\text{ cm}^{-1}$), and 1, 3, 5-trisubstituted compounds ($690 \pm 2\text{ cm}^{-1}$) arises from the out-of-plane deformation mode (ΦCC) of the benzene ring (Fig. II-45 *v*). As shown, this band is of special value for the characterization of the type of substitution in aromatic compounds. A second out-of-plane deformation of the ring (Fig. II-43) occurs in the 400 cm^{-1} region. Technical improvement of the existing spectrometers, allowing the investigation of low frequency regions, will probably enable the detection of new characteristic absorptions of aromatic compounds. These should arise from the participation of the substituent-ring bond vibration, which is thought to be appreciable [230, 248, 249]. Table II-51 shows the frequencies of some benzene derivatives in the $250\text{--}650\text{ cm}^{-1}$ region.

Table II-51 Frequencies of some monosubstituted benzenes in the $250\text{--}650\text{ cm}^{-1}$ region

| Compound | Frequency, cm^{-1} |
|---------------|---|
| Benzene | 610 <i>w</i> , 403 <i>vw</i> |
| Chlorobenzene | 616 <i>w</i> , 467 <i>s</i> , 415 <i>s</i> , 297 <i>s</i> |
| Bromobenzene | 615 <i>w</i> , 458 <i>vs</i> , 314 <i>m</i> |
| Toluene | 683 <i>w</i> , 521 <i>w</i> , 465 <i>s</i> , 347 <i>m</i> |

f. **Characteristic absorptions in the $1660\text{--}2000\text{ cm}^{-1}$ region.** Combination bands and *overtone*s of γCH vibrations in the $680\text{--}1000\text{ cm}^{-1}$ region occur

with low intensities in the $1660\text{--}2000\text{ cm}^{-1}$ range [250--252]. As shown, the bands in the region $680\text{--}900\text{ cm}^{-1}$ are characteristic for various types of substitution (see page 205); consequently, the corresponding overtones and combination bands have a typical pattern which can be correlated to the mode of substitution of the aromatic ring. Like their fundamentals, these bands are not influenced by the nature of substituents.

In general, aromatic compounds show more bands in the $1660\text{--}2000\text{ cm}^{-1}$ region than the majority of other organic compounds. However, these bands are weak ($\epsilon^{(e)} \approx 5$), and in order to study this region, it is necessary to work with liquid films of considerable thickness (0.1 mm) or with thick layers (1 mm) of concentrated solutions (ca. 10%). In the latter case one must take into account that absorption arising from solvent must be compensated correctly.

Figure II-53 shows the characteristic aspect of aromatic absorptions in the $1660\text{--}2000\text{ cm}^{-1}$ region. The simpler pattern in more symmetrical or more substituted compounds is due to the decrease of active γCH fundamental frequencies.

With regard to the origin and meaning of these bands, one can consider that their number and intensity are of greater analytical value than their positions. Spectra of monosubstituted compounds always show four bands with intensities decreasing towards lower frequencies. Small exceptions are seen in chloro- and bromobenzene, phenol etc., where band positions and intensity distribution are changed. However, the changes are small, and the general pattern of the region is very similar to the standard (see Fig. II-53). It should be pointed out that changes in position and intensity due to some substituents do not result in patterns similar to those characteristic for other types of substitution. Generally, the standard characteristics of the pattern are maintained.

The $1660\text{--}2000\text{ cm}^{-1}$ region may lose its analytical value because of either the occurrence of other fundamentals and overtones or the influence of some substituents. The most important fundamental occurring in the $1660\text{--}2000\text{ cm}^{-1}$ region is that arising from the carbonyl group. The $\nu\text{C=O}$ band is very strong and covers this region almost completely. The occurrence of an

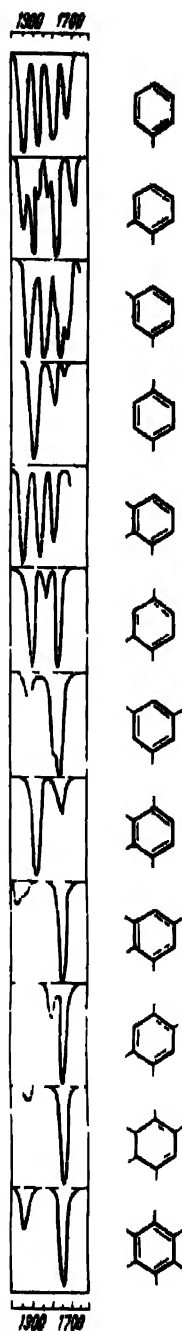


Fig. II-53 Characteristic pattern of the $1660\text{--}2000\text{ cm}^{-1}$ region in substituted monocyclic aromatic compounds.

interfering overtone, e.g., the overtone of the 910 cm^{-1} fundamental in styrene (see page 175), is generally readily recognizable and does not interfere with the analysis. In the case of monosubstituted fluoro compounds, ethers, or nitro-compounds, the pattern of the region changes appreciably; however, it does not become similar to that of other types of substitution and does not lead to confusion.

In order to use efficiently the $1660\text{--}2000\text{ cm}^{-1}$ region, it is recommended that each laboratory record the characteristic patterns of various substitution types with its own equipment.

g. CH vibrations in side chains of alkylbenzenes. CH stretching vibrations of methyl and methylene groups in side chains occur at normal alkane frequencies. An exception is the CH_3 group directly attached to the aromatic

Table II-53 Saturated νCH frequencies (cm^{-1}) in alkylbenzenes

| Compound | νCH , sym | νCH , asym | νCH_3 |
|---------------------------|----------------------|-----------------------|------------------|
| Toluene | 2867 | 2919 | |
| <i>o</i> -Xylene | 2851 | 2919 | |
| <i>m</i> -Xylene | 2856 | 2915 | |
| <i>p</i> -Xylene | 2865 | 2916 | |
| Ethylbenzene | 2890 | 2968 | 2930 |
| Isopropylbenzene | 2864 | 2971 | 2923 |
| <i>Tert</i> -Butylbenzene | 2870 | 2962 | |

ring. The frequency of the asymmetrical stretching mode is $30\text{--}40\text{ cm}^{-1}$ lower than in alkanes; the frequency of the symmetrical stretching is lowered by $7\text{--}10\text{ cm}^{-1}$ [222]. νCH frequencies of CH_3 and CH_2 groups for a number of alkylbenzenes are shown in Table II-52.

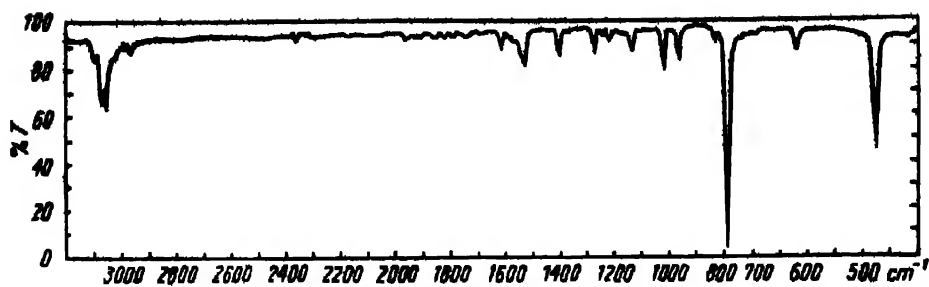
2. Polycyclic Aromatic Hydrocarbons

The large number of polycyclic aromatic hydrocarbons precludes their treatment as a single class. The relationships established in studies of spectra of monocyclic compounds cannot be extrapolated to the polycyclic ones because of the complexity and diversity of their structure. UV spectra were studied more extensively than IR. They provide reliable criteria for the characterization of the condensed systems and of some particular structural aspects.

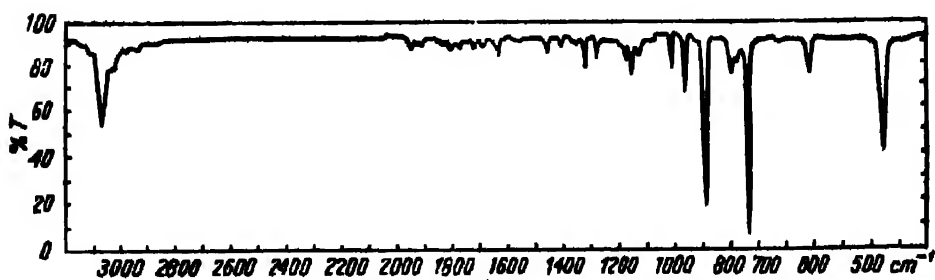
Some characteristic bands do appear, however, in the infrared in the regions $3000\text{--}3100\text{ cm}^{-1}$, $1500\text{--}1600\text{ cm}^{-1}$, and $650\text{--}900\text{ cm}^{-1}$ [253]. Spectra of some typical polycyclic hydrocarbons are shown in Fig. II-54.

The characteristic pattern of the deformation mode region at $650\text{--}900\text{ cm}^{-1}$ should be pointed out. The number of bands varies with the structure of the hydrocarbon [251, 253]. Naphthalene [255] has a strong band at 780 cm^{-1} . Anthracene with three linearly condensed rings has two strong bands, 725 and 880 cm^{-1} [256–258]. Phenanthrene also has two bands, 735 cm^{-1} and 810 cm^{-1} .

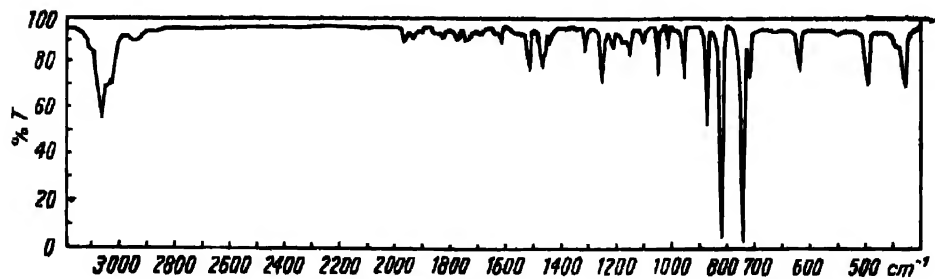
In a number of compounds with a 1,2-benzanthracene skeleton (114) a constant band at 890 cm^{-1} is observed. It is considered to be characteristic for compounds with an central anthracene skeleton (by analogy with the



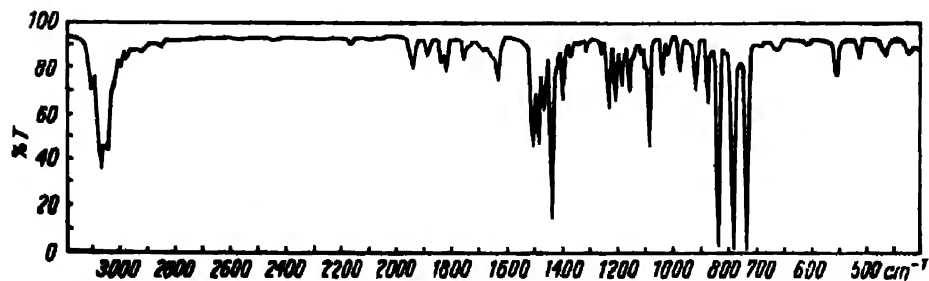
(a)



(b)



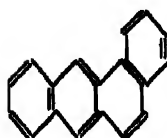
(c)



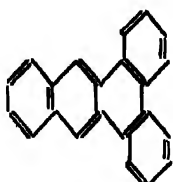
(d)

Fig. II-54 Infrared spectra of some polycyclic aromatic hydrocarbons:

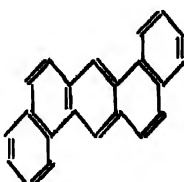
875 cm^{-1} sequence in 1,2,4,5-tetrasubstituted benzenes). 1,2,3,4-Dibenzanthracene (115), 1,2,5,6-dibenzanthracene (116), and 1,2,6,7-dibenzanthracene (117) with a central anthracene skeleton, all have a band at 890 cm^{-1} . This absorption does not occur in polycondensed aromatic systems which do not have an anthracene skeleton (e.g. chrysene, 1, 2, 5, 6-dibenzo-



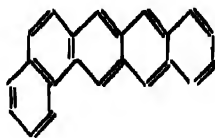
(114)



(115)



(116)



(117)

phenanthrene, and 1,2- and 3,4-benzofluorene). 9, 10-Dihydrophenanthrene, with a weak absorption at this frequency [253, 259, 260], is an exception.

In a series of methylnaphthalenes [261–263] infrared spectra were used for identification of the compounds. The out-of-plane deformation frequency γCH in α - and β -monosubstituted naphthalenes with electron-donating or electron-attracting substituents does not show any variations [264]. Relationships have been established between ring frequencies and the degree and type of substitution [261].

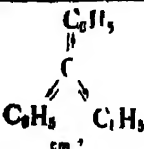
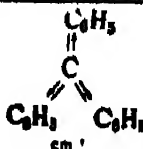
The pattern of the 650–1000 cm^{-1} region in spectra of compounds substituted with alkyl groups suggest, as in the case of monocyclic hydrocarbons, the existence of a relationship between the number and position of bands and the number and position of hydrogen atoms attached to the ring. However, the existing evidence is not sufficient to confirm this hypothesis [253, 259–261].

3. Compounds with triphenylmethane skeleton

Investigation of compounds containing the $(\text{C}_6\text{H}_5)_3\text{C}$ group has shown the constant appearance of a medium intensity band at 1179–1190 cm^{-1} and of a weak band at 1270–1290 cm^{-1} [267–269]. These absorptions were assigned to stretching vibrations of the $\text{C}-\text{C}_6\text{H}_5$ band by analogy with the symmetrical (in-phase) and asymmetrical (out-of-phase) stretching vibrations of the $\text{C}(\text{CH}_3)_3$ groups [270]. The frequencies of these bands are shown in Table II-53. $(\text{C}_6\text{H}_5)_3\text{C}-\text{D}$ shows bands at 1191 cm^{-1} and 1283 cm^{-1} [271].

In *tert*-butyl halides the frequency of the first band decreases by 50–70 cm^{-1} cf. the corresponding hydrocarbons; the frequency of the second band decreases by 10–20 cm^{-1} . In $(\text{C}_6\text{H}_5)_3\text{C}-\text{Cl}$ no such shifts are observed. In the spectrum of $(\text{C}_6\text{H}_5)_3\text{C}-\text{C}(\text{C}_6\text{H}_5)_3$ the band at 1280 cm^{-1} could not be identified [269]. The $\nu\text{C}-\text{C}_6\text{H}_5$ band position is influenced by the solvent [272]. The 1179–1190 cm^{-1} can be considered characteristic. The absence of this band shows that the molecule does not contain the $\text{C}_6\text{H}_5-\text{C}$ group.

Table II-53 Frequencies of $\nu_{C-C_6H_5}$ bands in the 1150–1300 cm^{-1} region

| Compound |  |  |
|--------------------------------|---|---|
| | cm^{-1} | cm^{-1} |
| $(C_6H_5)_3C-H$ | 1184 | 1290 |
| $(C_6H_5)_3C-OH$ | 1179 | 1270 |
| $(C_6H_5)_3C-Cl$ | 1184 | 1284 |
| $(C_6H_5)_3C-CH_3$ | 1184 | 1282 |
| $(C_6H_5)_3C-CH_2Cl$ | 1185 | 1280 |
| $(C_6H_5)_3C-COCl$ | 1190 | 1278 |
| $(C_6H_5)_3C-CH_2-CH_2Cl$ | 1187 | 1273 |
| $(C_6H_5)_3C-(CF_3)_2Cl$ | 1186 | 1282 |
| $(C_6H_5)_4C$ | 1186 | 1280 |
| $(C_7H_5)_3C-CH_2-CH_2-C_6H_5$ | 1186 | 1272 |

D. ORGANIC CATIONS

1. Carbonium ions

Carbonium ions have a carbon atom with sp^2 hybridization and a vacant p orbital (Fig. II-55). According to quantum mechanical theory such ions are planar. For some simple alkylcarbonium ions, the normal vibration modes have been calculated [273, 274] and frequencies were assigned. In *tert*-butyl (118), *tert*-amyl (119), isopropyl (120) carbonium ions, and the corresponding perdeuterated derivatives, the infrared absorption bands correspond to those calculated for a planar model. The *tert*-butyl cation has a C_{3v} symmetry (118 a), and the isopropyl cation has C_{2v} symmetry (120 a).

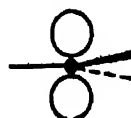
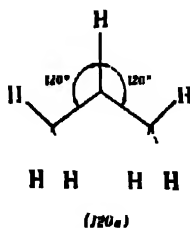
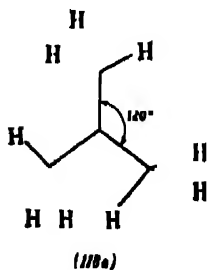
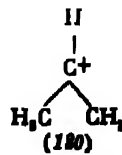
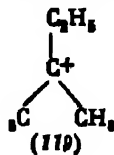
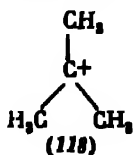


Fig. II-55 Tertiary carbonium ion.



The spectra were recorded in excess SbF_5 . The complex $\text{R}_3\text{C}^+\text{SbF}_6^-$ was obtained in the following way:

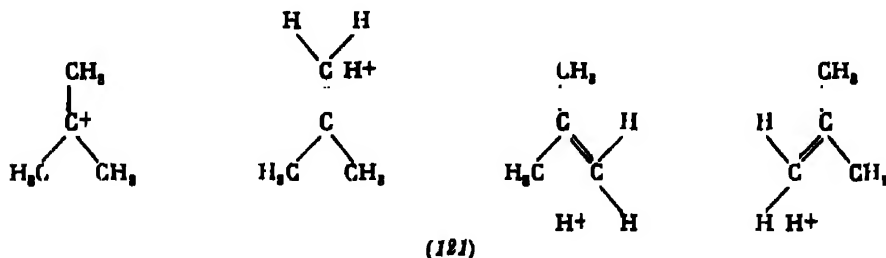


The assignment of bands in spectra of *tert*-butyl and perdeuterio*tert*-butyl-hexafluoroantimonates are shown in Table II-54.

Table II-54 Frequencies of the *t*-butyl cation in $(\text{CH}_3)_3\text{C}^+\text{SbF}_6^-$ and $(\text{CD}_3)_3\text{C}^+\text{SbF}_6^-$ [273]

| Frequencies, cm^{-1} | | Assignments |
|-------------------------------|-----------------------------|--------------------------------------|
| $(\text{CH}_3)_3\text{C}^+$ | $(\text{CD}_3)_3\text{C}^+$ | |
| 2830 s | 2062 s | CH_3 stretching mode |
| 2500 w | | combination mode ($\nu_3 + \nu_9$) |
| 1455 w | 1050 vw | CH_3 deformation mode |
| 1290 vs | 1330 s | asym C—C—C stretching mode |
| 1070 m | | in-plane rocking CH_3 |
| 962 mw | | in-plane rocking CH_3 |
| 1300 overlap | 955 s | CH_3 deformation mode |

The νCH frequency is unusually low while the frequency of the asymmetrical skeletal vibration is unusually high. These characteristics were partly attributed to resonance (structures (121)) which results in a lowering of the C—H bond force constant and an increase in bond strength of the C—C bond [273].

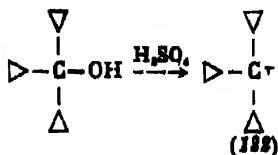


For the isopropyl cation in $(\text{CH}_3)_2\text{CH}^+\text{SbF}_6^-$, the assignments of frequencies are shown in Table II-55.

Table II-55 Frequencies of the isopropyl cation in $(\text{CH}_3)_2\text{CH}^+\text{SbF}_6^-$ and $(\text{CD}_3)_2\text{CH}^+\text{SbF}_6^-$ [273]

| Frequencies, cm^{-1} | | Assignments |
|-------------------------------|------------------------------|--------------------------------|
| $(\text{CH}_3)_2\text{CH}^+$ | $(\text{CD}_3)_2\text{CH}^+$ | |
| 2730 s | 2013 s | CH_3 stretching modes |
| 1490 s | 930 s | CH in-plane deformation modes |
| 1260 s | 1378 s | asym C—C—C stretching modes |
| 1175 w | | |
| 940 vw | | |

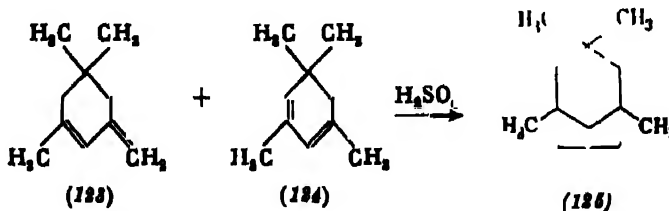
In the tricyclopropyl carbonium ion (122), obtained from tricyclopropyl carbinol and concentrated sulfuric acid, the characteristic vibrations give rise to strong absorptions at 837, 1279, and 1445 cm^{-1} [275].



Alkenyl cations formed in reactions of dienes with sulfuric acid contain the conjugated allylic system

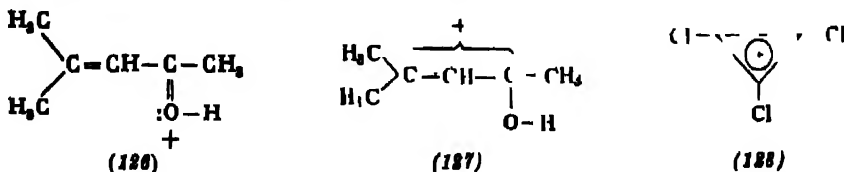


The spectrum of the carbonium ion formed on treatment of the mixture of dienes (123) and (124) with concentrated sulfuric acid shows a single strong band at 1533 cm^{-1} assigned to the unsaturated system in (125).



The absorption occurs at a position intermediate between the frequency of a simple C—C bond and that of a C=C double bond. The intensity of the band is about ten-fold that of conjugated double bonds.

The main contribution of the allylic structure (127) in protonated α , β -unsaturated ketones has been demonstrated in the case of 4-methyl-3-pentenone-2·H⁺ (126) by the existence of a strong absorption at 1540 cm^{-1} [276], corresponding to the alkenyl cation (1533 cm^{-1}).



A second band, occurring at 1595 cm^{-1} in protonated ketones has also been assigned to the stretching vibration of the allylic system, although absorptions between 1590—1610 cm^{-1} also occur in other protonated ketones, including acetone, dicyclopropylketone, etc [276].

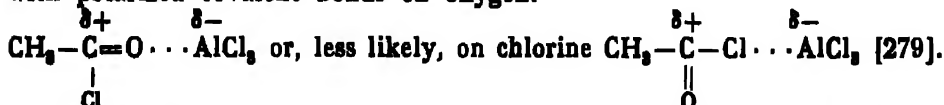
The spectrum of the stable trichlorocyclopropenyl cation (129) (isolated as $\text{C}_3\text{Cl}_3^+\text{AlCl}_4^-$ and $\text{C}_3\text{Cl}_3^+\text{SbCl}_6^-$) with trigonal symmetry D_{3h} shows three

absorption bands, at 1350, 1315, and 731 cm^{-1} in $\text{C}_6\text{Cl}_6^+ \text{AlCl}_4^-$ and 1343, 1313, and 735 cm^{-1} in $\text{C}_6\text{Cl}_6^+ \text{SbCl}_6^-$. A fourth band occurring at 482 cm^{-1} is observed only in the complex with AlCl_3 . This band is assigned to the anion AlCl_4^- (481 cm^{-1}) [277].

2. Oxocarbonium ions

Structures of intermediate complexes formed from acid chlorides and Friedel-Crafts catalysts (AlCl_3 , BF_3 , FeCl_3 , SnCl_4 , SbCl_5 , ZnCl_2) have been investigated by a variety of spectroscopic methods, including infrared spectroscopy. The presence of two functional groups in acid halides (the $\text{C}=\text{O}$ group and the Cl atom) suggested several possibilities for the structure of the intermediate [278].

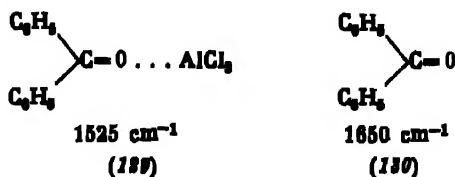
In the complex between CH_3COCl and AlCl_3 , two structural types have been considered: ion pairs $[\text{CH}_3\text{CO}^+][\text{AlCl}_4^-]$ and donor-acceptor complexes with polarized covalent bonds on oxygen.



Study of infrared spectra of the system $\text{CH}_3\text{COCl} \cdot \text{AlCl}_3$ showed the existence of both types of intermediates: donor-acceptor complex in solvents of low dielectric constant and ion pairs in solvents of high dielectric constant or in the solid state [279]. In acetyl chloride CH_3COCl the stretching vibration of the $\text{C}=\text{O}$ bond has a frequency of 1807 cm^{-1} [280]. In the liquid complex $\text{CH}_3\text{COCl} \cdot \text{AlCl}_3$, the νCO frequency is 1637 cm^{-1} , 170 cm^{-1} lower. This proves the existence of a carbonyl group perturbed by the formation of a donor-

acceptor bond $\text{R}-\overset{\delta+}{\underset{\text{Cl}}{\text{C}}}=\overset{\delta-}{\text{O}}\cdots\text{AlCl}_3$. Shifts in the same direction, but slightly

smaller (125 cm^{-1}) also have been observed in complexes of ketones with AlCl_3 ; for example, in the complex of benzophenone with AlCl_3 (129), the $\nu\text{C}=\text{O}$ falls from 1650 cm^{-1} in (130) to 1525 cm^{-1} [281].

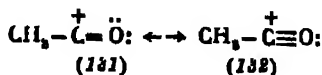


In the infrared spectrum of the ionized complex $[\text{CH}_3\text{CO}^+][\text{AlCl}_4^-]$ formed in the reaction



the strong bands at 2307 cm^{-1} and 2203 cm^{-1} were assigned to the acylium ion [280]. The increased frequency of the $\text{C}=\text{O}$ group cf. normal ketones was explained by the increase in bond order of the carbon - oxygen bond due to the

positive charge. The observed frequency corresponds to the resonance structures (131) and (132).



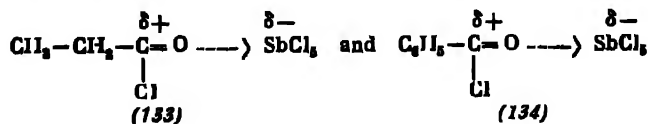
The frequency 2300 cm^{-1} was assigned to this band [280]. The origin of the band arising at 2203 cm^{-1} is less certain; it was assigned to complexes $\text{CH}_3-\overset{+}{\text{C}}=\text{O} \cdots [\text{Cl}-\text{AlCl}_3]^-$ or $\text{CH}_3-\overset{+}{\text{C}}=\text{O} \cdots [\text{AlCl}_3]\text{Cl}^-$. In the case of the complex $\text{CH}_3\text{COCl} \cdot \text{GaCl}_3$, reverse assignments were proposed [282].

The structure of the complex depends on the nature of the acid halides and the Lewis acid. Studies of infrared spectra of solid complexes have shown that the formation of a crystalline complex does not prove the existence of an acylium ion. In the system $\text{CH}_3\text{COF} \cdot \text{BF}_3$ at low temperature, the ionized complex $\text{CH}_3\text{CO}^+\text{BF}_4^-$ is predominantly formed, with a strong band at 2300 cm^{-1} [283, 284]. In many complexes of acetyl, propionyl, and benzoyl fluorides with BF_3 , SbF_5 , AsF_5 , the bands in the $\text{C}=\text{O}$ donor-acceptor region are practically absent, and strong absorptions occur at ca. 2300 cm^{-1} [283]. These complexes are thought to have predominantly an acylium ion structure Table II-56).

Table II-56 Characteristic frequencies in complexes RCOF^+ Lewis acids, cm^{-1} [283]

| Compound | $\nu\text{C}=\text{O}$ | $\nu\text{CH}_3\text{CO}^+$ | $\nu\text{C}-\text{F}$ |
|---|-----------------------------|-----------------------------|------------------------|
| CH_3COF | 1848 <i>vs</i> | — | 826,809 <i>s</i> |
| $\text{CH}_3\text{CO}^+\text{BF}_4^-$ | 1619 <i>m</i> 1560 <i>w</i> | 2229 <i>vs</i> | — |
| $\text{CH}_3\text{CO}^+\text{SbF}_6^-$ | 1621 1554 <i>s</i> | 2294 <i>vs</i> | — |
| $\text{CH}_3\text{CO}^+\text{AsF}_6^-$ | 1620 <i>w</i> 1558 <i>w</i> | 2302 <i>vs</i> | — |
| $\text{CH}_3\text{CH}_2\text{COF}$ | 1845 <i>vs</i> | — | 805 <i>s</i> |
| $\text{CH}_3\text{CH}_2\text{CO}^+\text{SbF}_6^-$ | 1610 <i>m</i> | 2290 <i>vs</i> | — |
| $\text{CH}_3\text{CH}_2\text{CO}^+\text{AsF}_6^-$ | 1608 <i>w</i> | 2289 <i>vs</i> | — |
| $\text{C}_6\text{H}_5\text{COF}$ | 1812 <i>vs</i> | — | 1020 _s |
| $\text{C}_6\text{H}_5\text{CO}^+\text{SbF}_6^-$ | 1531 <i>m</i> | 2212 <i>vs</i> | — |
| $\text{C}_6\text{H}_5\text{CO}^+\text{AsF}_6^-$ | 1546 <i>m</i> | 2228 <i>vs</i> | — |

Infrared absorptions have shown that in complexes $\text{CH}_3\text{COCl} \cdot \text{SbCl}_5$ ionized species $\text{CH}_3\text{CO}^+\text{SbCl}_6^-$ are predominant, while complexes of propionyl chloride $\text{CH}_3\text{CH}_2\text{COCl} \cdot \text{SbCl}_5$ (133) and benzoyl chloride $\text{C}_6\text{H}_5\text{COCl} \cdot \text{SbCl}_5$ (134) are mainly of the donor-acceptor type [283].



It was shown that in many 1:1 complexes of acetyl chloride with Lewis acids, both forms are present [283-288]. In the complex $\text{CH}_3\text{COCl} \cdot \text{TiCl}_4$,

the $\nu\text{C}=\text{O}$ frequency of acetyl chloride falls from 1802 cm^{-1} to 1620 cm^{-1} ($\Delta\nu=180\text{ cm}^{-1}$), and in propionyl chloride, from $1780\text{--}1840\text{ cm}^{-1}$ to 1650 cm^{-1} . The calculated force constants fit the assigned structures. The C-halogen band disappears on complex formation.

Table II-57

| Vibration | CH_3COCl | Complex with AlCl_3 |
|-------------------------|--------------------------|---------------------------------|
| νCH_3 , asym | 3012 | 2941 |
| νCH_3 , sym | 2960 | 2874 |

The frequency of the CII_3 group. The νCH_3 frequency decreases due to the ionic structure of the molecule [274]. νCH_3 frequencies in acetyl chloride and in its complexes with aluminium chloride are shown in Table II-57.

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CHAPTER 2

HALOGEN COMPOUNDS

Mono- and polyhalogenated compounds are formally derived from hydrocarbons, by substitution of one or several hydrogen atoms with fluorine, chlorine, bromine, or iodine.

Compared to C—H bonds, C—X bonds (X=F, Cl, Br, I) have much lower frequencies because of increased reduced masses of the atoms and decreased force constants.

The frequency of stretching vibrations $\nu\text{C—Cl}$, $\nu\text{C—Br}$, and $\nu\text{C—I}$ lies in the range 500–800 cm^{-1} . The C—F bond is an exception, its vibrations occurring at 1000–1400 cm^{-1} . The approximate limits are

| | | | |
|----------------------------|--------------------------|--------------------------|-------------------------|
| $\nu\text{C—F}$ | $\nu\text{C—Cl}$ | $\nu\text{C—Br}$ | $\nu\text{C—I}$ |
| 1000–1400 cm^{-1} | 600–800 cm^{-1} | 500–600 cm^{-1} | <500 cm^{-1} . |

The C—X frequency decreases with increasing atomic mass of the halogen.

In chlorinated compounds the position of absorption bands varies within a relatively large range. This range is narrower in bromides and even more so in iodides. In fluorides the variations are particularly large. Fluorides differ from the other halides by their chemical properties as well.

C—X deformation vibrations have very low frequencies. Absorption bands occur in a region less accessible to usual techniques and have not been sufficiently studied. The electronegativity of the halogen atoms and the presence of unshared electrons make the C—X bond much more sensitive to structural and medium changes. For the same reason halogen atoms have a strong influence on the vibrations of adjacent bonds in the molecule.

The existence of very simple and accurate methods for the determination of halogens in organic compounds, along with the fact that vibrations of C—X bonds are less characteristic than those of other functional groups, confines the infrared spectroscopy of this class of compounds to problems of molecular structure.

1. Haloalkanes

The lower members of the homologous series of halogenated alkanes have been subjected to a great number of theoretical studies [1]. Most extensively investigated was methyl chloride; methyl fluoride, bromide, and iodide and their perdeutero derivatives have been less studied. As expected, the spectra of these compounds are very similar to that of methyl chloride.

Methyl chloride CH_3Cl belongs to the point group C_{3v} and has six normal vibration modes (Fig. II-56 and Table II-58). All are active in Raman and the infrared. Three modes are totally symmetrical (A_1), and three are doubly degenerate (E). Any other, less symmetrical model would have nine fundamental vibrations active in the infrared. Totally symmetrical vibrations ν_1 , ν_2 ,

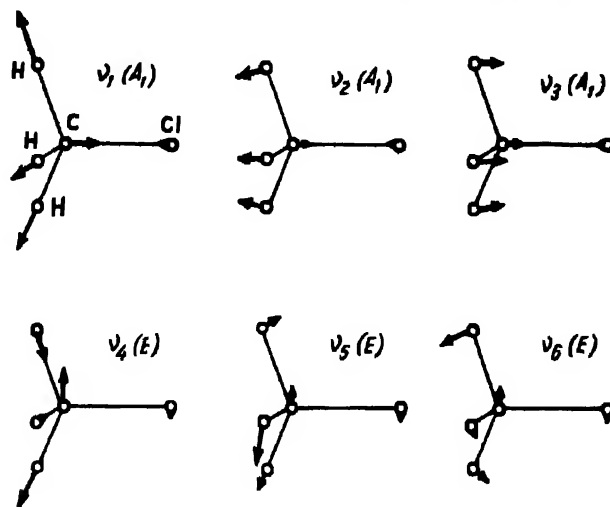


Fig. II-56 Normal vibration modes of the methyl chloride molecule (point group C_{3v}).

and ν_3 give rise to *parallel* bands, while the doubly degenerate vibrations give rise to *perpendicular* bands (see page 104). The infrared spectrum shows four strong parallel bands, but it is very likely that absorptions at 2878.8 cm^{-1} and 2966.2 cm^{-1} are components of a doublet due to a Fermi resonance involving the first overtone of the 1453.2 cm^{-1} band. In this case the doublet cor-

Table II-58 Fundamental frequencies in CH_3Cl (vapor) [1]

| Frequency ν , cm^{-1} | Vibration | Species | Vibration type |
|------------------------------------|-----------|---------|-------------------------|
| 732.1 \parallel (vs) | ν_1 | A_1 | $\nu\text{C}-\text{Cl}$ |
| 1015.0 \perp (m) | ν_2 | E | |
| 1354.9 \parallel (s) | ν_3 | A_1 | δCH_3 |
| 1454.6 \perp (m) | ν_4 | E | δCH_3 |
| 2966.2 \parallel (vs) | ν_5 | A_1 | νCH |
| 3041.8 \perp (s) | ν_6 | E | νCH |

responds to a single fundamental frequency. With this assumption all combination bands in the methyl chloride spectrum can be explained [1].

Comparing the fundamental vibrations of the four methyl halides, one can observe that the ν_3 vibration frequency decreases going from CH_3F to CH_3I .

This shows that the ($\nu\text{C}-\text{X}$) assignment is correct. The force constant of the bond decreases in the same order (see Table II-59).

Table II-59 Vibration frequencies and force constants of C-X bonds [2]

| Halide | CH_3-F | CH_3-Cl | CH_3-Br | CH_3-I |
|----------------------------------|------------------------|-------------------------|-------------------------|------------------------|
| $\nu \text{ cm}^{-1}$ | 1048 | 710 | 595 | 525 |
| $k \cdot 10^{-8} \text{ dyn cm}$ | 5.10 | 3.12 | 2.62 | 2.16 |

Fundamental vibrations in polychlorinated derivatives of methane (methylene chloride CH_2Cl_2 , chloroform CHCl_3 , and carbon tetrachloride CCl_4) have also been identified [1]. 1,2-Dihaloethanes and 1,1,2,2-tetrahaloethanes are classical examples of molecules where conformational isomerism has been pointed out by means of spectral analysis [3-8]. Theoretically, in 1,2-dichloro- and 1,2-dibromoethane, restricted rotation about the C-C bond should give rise to three eclipsed conformations (one *syn*- C_{2v} and two equivalent *anti*- C_2) [9] (Fig. II-57).

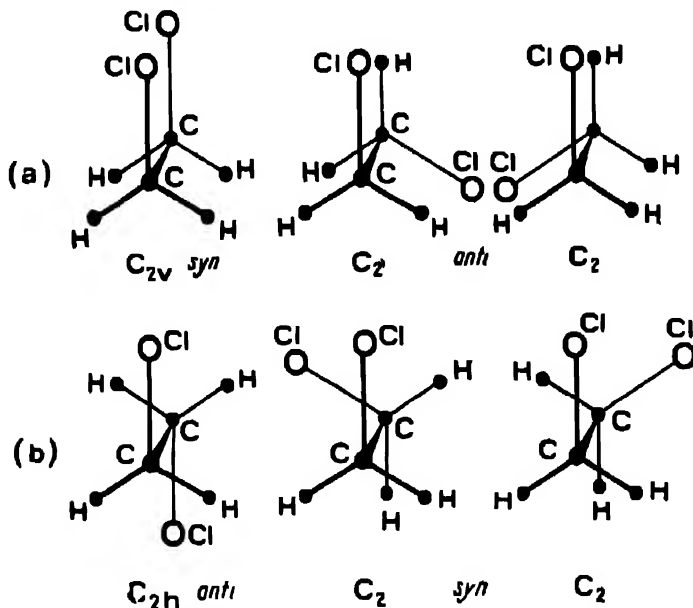


Fig. II-57 Conformations of dichloroethane:
(a) eclipsed; (b) staggered.

Being enantiomers, the *anti*-forms have identical spectra. In these forms all vibrational modes are active both in the infrared and in Raman. In the eclipsed *syn*-conformation with C_{2v} symmetry, coincidences for all vibrations but those of the A_1 class are allowed. For the staggered *anti*-conformation

with C_{2h} symmetry, the mutual exclusion rule forbidding all coincidences is applicable. The staggered *syn* forms are enantiomers. Studies of infrared spectra at different temperatures have shown that at low temperatures the staggered *anti* form is stable, while at normal temperature a mixture of staggered *anti* and *syn* forms are present. In 1,2-dichloroethane the staggered *anti* conformation (C_{2h}) was assigned the 1291 cm^{-1} band and the *syn* form (C_2) was assigned the 1235 cm^{-1} band. Studies of intensity variations of these bands with temperature lead to the conclusion that at normal temperature the liquid mixture contains ca. 70% *anti* isomer [4] (Fig. II-58).

C-Hal stretching vibration. Comparative studies of infrared spectra of primary, secondary, and tertiary alkyl halides have shown that the frequency of this vibration depends on the structure of the carbon atom attached to the halogen [10] (Table II-60).

The C-X frequencies of methyl halides are $25\text{--}55\text{ cm}^{-1}$ higher than those of ethyl halides. The different behavior of the first member of the series is also common in other functional groups. In the series ethyl, isopropyl, and *tert*-butyl halides, the frequency decreases by 86 cm^{-1} in chlorides, 46 cm^{-1} in bromides, and 10 cm^{-1} in iodides. The vibration of the C-X bond is complicated, being strongly influenced by the molecular structure adjacent to the bond. In this class of compounds, it was difficult to establish reliable relationships between molecular structure and frequencies of the carbon-halogen bond because spectra of higher alkyl halides are complicated by interactions of C-X vibrations with vibrations arising from the rest of the molecule. A further complication is the increased number of bands due to conformational isomers.

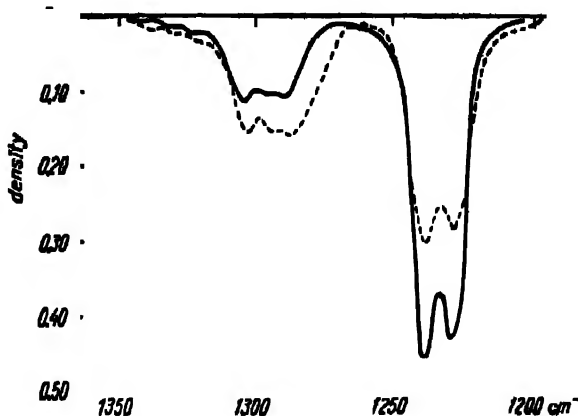


Fig. II-58 Temperature dependence of the ratio of conformational isomers in dichloroethane. Solid line — the spectrum at 151°C ; dotted line — the spectrum at 25.6°C [4].

Table II-60 Frequencies of the C-X bond, cm^{-1}

| Alkyl halide | X= | Cl | Br | I |
|--|----|-----|-----|-----|
| $\text{CH}_3\text{CH}_2\text{--X}$ | | 656 | 560 | 500 |
| $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH--X} \end{array}$ | | 615 | 536 | 495 |
| $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{C--X} \\ \\ \text{CH}_3 \end{array}$ | | 570 | 514 | 490 |

In some alkyl halides with more than two carbon atoms, a doubling of bands in the C—X stretching mode region was observed. From the very beginning the phenomenon was assigned to the existence of two or several conformational isomers [11, 12]. Recent systematic studies of many primary, secondary, and tertiary alkyl chlorides enabled the establishment of a reliable relationship between the absorption of C—Cl bonds and the stereochemistry of these compounds [13].

In primary alkyl chlorides, as a result of free rotation about the C—C bond linking the CH_2Cl group to the rest of the chain, three conformational isomers are possible. Two are enantiomers and cannot be distinguished spectroscopically. Distinct C—Cl bands will thus exist only for two isomeric forms.

In Figs. II-59—II-61 primary, secondary, and tertiary chlorides have been labeled *P*, *S* and *T*, respectively [14]. The subscript *H* corresponds to the conformation in which the chlorine atom is *trans* to a hydrogen atom and subscript *C* represents a chlorine atom *trans* to a carbon atom.

Ethyl chloride exists in a single conformation P_H (Fig. II-59). The infrared spectrum shows a single $\nu\text{C—Cl}$ band at 657 cm^{-1} . Neopentyl chloride exists only in the P_C conformation. Its spectrum shows a single $\nu\text{C—Cl}$ band at 723 cm^{-1} . Isobutyl chloride with a CH_3 group in the α -position to the chlorine atom is a typical case in which one P_H conformation and two enantiomeric P_C conformations can occur. Consequently, two bands will arise in the infrared spectrum. The 730 cm^{-1} band is assigned to the P_C conformation (by analogy with straight chain primary alkyl chlorides). The second band arises at 686 cm^{-1} , 35 cm^{-1} higher than in a normal P_H con-

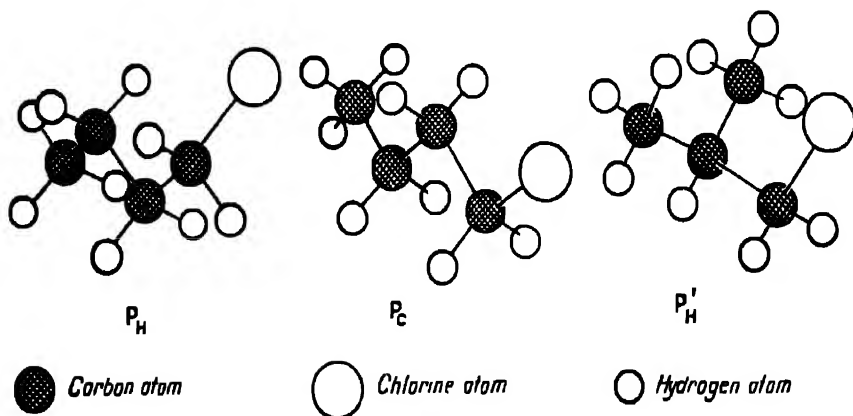


Fig. II-59 Conformations of 1-chlorobutane [13].

formation. The shifting of the band towards higher frequencies is observed in other alkyl chlorides branched at the α -position and is considered to be characteristic for this structure. This conformation is labeled P'_H to be distinguished from the P_H conformation, possible only in molecules with at

least one CH_2 group between the CH_2Cl group and the rest of the molecule (see Table II-61).

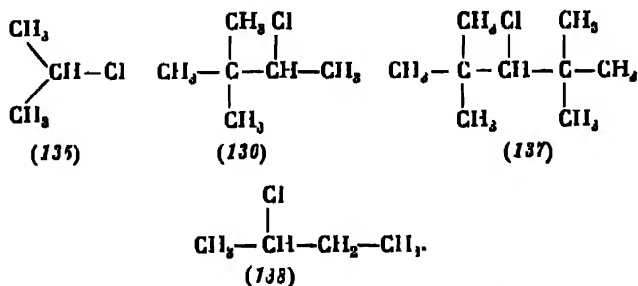
Table II-61 $\nu\text{C}-\text{Cl}$ frequencies in primary alkyl chlorides (cm^{-1}) [13]

| Chloride | Conformation | | |
|---|--------------|--------|---------|
| | P_C | P'_H | P_H |
| $\text{CH}_3-\text{CH}_2\text{Cl}$ | — | — | 657 s |
| $(\text{CH}_3)_2\text{C}-\text{CH}_2\text{Cl}$ | 723 s | — | — |
| $(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{Cl}$ | 730 s | 686 s | — |
| $\text{CH}_3(\text{CH}_2)_2\text{Cl}$ | 730 | — | 646 |
| $\text{CH}_3(\text{CH}_2)_3\text{Cl}$ | 730 | — | 649 |
| $\text{CH}_3(\text{CH}_2)_n\text{Cl}$ ($n=4 \dots 6,15$) | 727 731 | — | 648–650 |
| $\text{CH}_3(\text{CH}_2)_2\text{CH}(\text{CH}_3)-\text{CH}_2\text{Cl}$ | 727 | 679 | — |
| $\text{CH}_3\text{CH}_2-\text{CH}-\text{CH}_2\text{Cl}$ $(\text{CH}_3)_2\text{C}-\text{CH}_3$ | 728 | 681 | — |
| $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CH}_2\text{Cl}$ | 728 | — | 653 |
| $\text{Cl}(\text{CH}_2)_4\text{Cl}$ | 731 | — | 648 |
| $\text{Cl}(\text{CH}_2)_5\text{Cl}$ | 736 | — | 648 |

Thus, in primary alkyl chlorides with the CH_2Cl group attached to a CH_2 group, the characteristic $\text{C}-\text{Cl}$ bands arise at 648 cm^{-1} and 730 cm^{-1} . They correspond to the conformations P_H and P_C . In primary alkyl chlorides with the CH_2Cl group attached to a carbon atom linked in turn to two other carbons and a hydrogen atom, the absorption at 680 cm^{-1} is assigned to the P'_H conformation and that at 730 cm^{-1} , to the P_C conformation.

In secondary chlorides the situation is more complicated. In this case one must consider conformations resulting from rotation about two neighboring $\text{C}-\text{C}$ bonds adjacent to the $\text{C}-\text{Cl}$ bond. The notations are S_{HH} , S_{CH} , S'_{HH} [13, 14] (Fig. II-60), and S_{CC} .

In the following four secondary chlorides only one conformation is possible:



2-Chloropropane (135) exists only in the S_{HH} conformation. Its spectrum shows a single band at 611 cm^{-1} in the $\text{C}-\text{Cl}$ stretching mode region. A band

arising at 608–612 cm^{-1} in secondary halides can thus be assigned to the S_{HH} conformation (Fig. II-60 and Table II-62).

2,2-Dimethyl-3-chlorobutane (136) can exist only in the S_{CH} conformation (Fig. II-60). The spectrum shows two bands in the C–Cl region, at

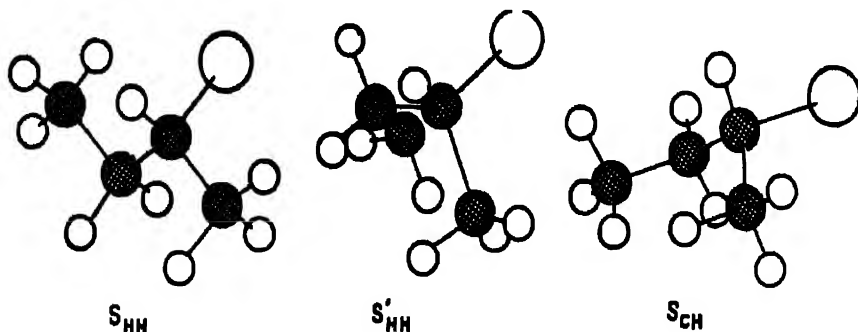


Fig. II-60 Conformations of 2-chlorobutane [13].

730 cm^{-1} and 667 cm^{-1} . It has been observed that a number of halides capable of existing in the S_{CH} conformation have bands in the range 655–672 cm^{-1} . The latter absorption is assigned to the S_{CH} conformation. The band at 730 cm^{-1} does not arise from a C–Cl vibration. 3-Chloro-2,2,4,4-tetramethylpentane (137) exists only in the S_{CC} conformation which is assigned the band at 758 cm^{-1} . The neighboring band at 733 cm^{-1} does not have an exact assignment. It is assumed that it arises from the vibration of the butyl group adjacent to the CHCl group. 2-Chlorobutane (138) has three bands: 671, 628, and 609 cm^{-1} and can occur in three conformations: S_{CH} , S_{HH} , and S'_{HH} (Fig. II-60).

The 671 cm^{-1} band is assigned to the conformation S_{CH} and the band at ca. 609 cm^{-1} to the conformation S_{HH} . The 628 cm^{-1} band (S'_{HH}) occurs in higher homologs as well; sometimes it is overlapped or appears only as a shoulder. This band is much clearer in bromides [15]. In tertiary chlorides (Table II-63) assignments are less certain. They can form four conformational isomers occurring from rotation about the C–C bond adjacent to the C–Cl bond. *tert*-Butyl chloride (139) has a single conformation T_{HHH} absorbing at 569 cm^{-1} . 2-Chloro-2-methylbutane (140) has two conformational isomers T_{HHH} and T_{CHH} (Fig. II-61). The spectrum of this compound shows two strong bands, ca. 560 cm^{-1} and 620 cm^{-1} .

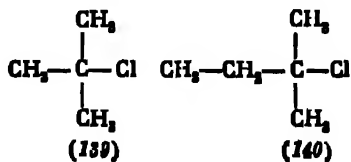


Table 11-62 $\nu\text{C}-\text{Cl}$ frequencies, cm^{-1} in secondary alkyl chlorides [13]

| Halide | Conformation (Fig. 11-60) | | | |
|--|---------------------------|----------|-----------|----------|
| | S_{CC} | S_{CH} | S'_{HH} | S_{HH} |
| $\begin{array}{c} \text{Cl} \\ \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array}$ | — | — | — | 611 s |
| $\begin{array}{c} \text{Cl} \\ \\ (\text{CH}_3)_2\text{C}-\text{CH}-\text{CH}_3 \end{array}$ | — | 667 | — | — |
| $\begin{array}{c} \text{Cl} \\ \\ (\text{CH}_3)_2\text{C}-\text{CH}-\text{C}(\text{CH}_3)_3 \end{array}$ | 758 | — | — | — |
| $\begin{array}{c} \text{Cl} \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$ | — | 671 m | 628 m | 609 s |
| $\begin{array}{c} \text{Cl} \\ \\ \text{CH}_3-\text{CH}-(\text{CH}_2)_2-\text{CH}_3 \end{array}$ | — | 670 m | — | 612 s |
| $\begin{array}{c} \text{Cl} \\ \\ (\text{CH}_3)_2\text{CH}-(\text{CH}_2)_2-\text{CH}_3 \end{array}$ | — | 672 m | — | 611 s |
| $\begin{array}{c} \text{Cl} \qquad \qquad \text{Cl} \\ \qquad \qquad \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_3 \end{array}$ | — | 678 m | 627 | 609 s |
| $\begin{array}{c} \text{Cl} \\ \\ \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_3 \end{array}$ | 749 m | 667 635m | 628 | 609 s |
| $\begin{array}{c} \text{Cl} \\ \\ \text{CH}_3-\text{CH}_2-\text{CH}-(\text{CH}_2)_2-\text{CH}_3 \end{array}$ | 753 m* | 663 m | 637 m | 608 m |
| $\begin{array}{c} \text{Cl} \\ \\ \text{CH}_3-(\text{CH}_2)_2-\text{CH}-(\text{CH}_2)_2-\text{CH}_3 \end{array}$ | 733 m* | 662 m | 635 m | 610 m |

* Overlapped with γCH_2 r

The 560 cm^{-1} band is assigned to the conformation T'_{HHH} by analogy with *tert*-butyl chloride, and the 620 cm^{-1} band, to the conformation T_{CHH} .

In other possible conformations, tertiary chlorides absorb at $500\text{--}550\text{ cm}^{-1}$ and $700\text{--}750\text{ cm}^{-1}$. The assignment of these bands is difficult.

Regions of characteristic absorptions in primary, secondary, and tertiary alkyl chlorides in various conformations are shown in Table 11-64.

In the homologous series of alkyl bromides, starting with ethyl bromide, two bands are observed in the C - Br region. They are assigned to conformational isomers present at equilibrium [12]. Although ethyl, isopropyl, and

Table II-48 ν_{C-Cl} frequencies (cm^{-1}) in tertiary alkyl chlorides [13]

| Halide | Conformation | | | |
|---|--------------|-----------|-----------|------------|
| | Unassigned | T_{CHH} | T_{HHH} | Unassigned |
| $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{Cl} \\ \\ \text{CH}_3 \end{array}$ | — | — | 569 | — |
| $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{Cl} \\ \\ \text{CH}_3 \end{array}$ | — | 620 | 560 | — |
| $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3(\text{CH}_2)_2-\text{C}-\text{Cl} \\ \\ \text{CH}_3 \end{array}$ | 746 | 632 | 572 | — |
| $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3-\text{C}-\text{C}-\text{Cl} \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array}$ | 743 | 611 | 569 | 508 |
| $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3(\text{CH}_2)_2-\text{C}-\text{Cl} \\ \\ \text{CH}_3 \end{array}$ | 734 | 617 | 570 | 540 |

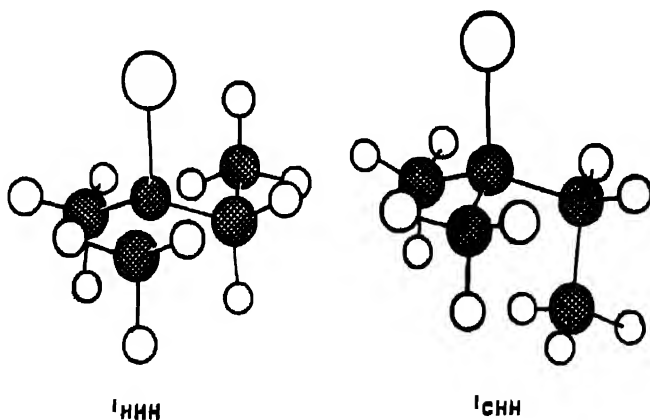


Fig. II-61 Conformation of tertiary chlorides [13].

Table II-64 $\nu\text{C}-\text{Cl}$ frequencies in alkyl chlorides [13]

| Primary alkyl chlorides | | Secondary alkyl chlorides | | Tertiary alkyl chlorides | |
|-------------------------|----------------------------|---------------------------|----------------------------|--------------------------|----------------------------|
| Conformation | Frequency cm^{-1} | Conformation | Frequency cm^{-1} | Conformation | Frequency cm^{-1} |
| P_R | 648-657 | S_{HH} | 608-617 | T_{HHH} | 560-581 |
| P'_H | 679-686 | S'_{HH} | 627-637 | | |
| P_C | 723-730 | S_{CH} | 655-674 | T'_{HHH} | 611-632 |
| | | S_{CC} | 758 | | |

tert-butyl bromides have a single type of conformation, the $\nu\text{C}-\text{Br}$ region of the corresponding spectra shows two bands (see Table II-65). The additional absorption arises from other causes. The most correct explanation is probable a Fermi resonance. Alkyl iodides have been studied less. They absorb around 500 cm^{-1} [16].

In phenylethyl bromide $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2\text{Br}$ and 1-phenyl-3-bromopropane

Table II-65 Characteristic $\nu\text{C}-\text{Br}$ frequencies in alkyl bromides [7, 12]

| Halide | Frequency in the $\nu\text{C}-\text{Br}$ region, cm^{-1} | | |
|---|---|-----|---------------------------|
| $\text{CH}_3-\text{CH}_2-\text{Br}$ | 681 | 565 | One possible conformation |
| $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Br}$ | 647 | 567 | |
| $\text{CH}_3(\text{CH}_2)_3-\text{Br}$ | 645 | 564 | |
| CH_3 \diagup $\text{CH}-\text{Br}$ | 678 | 543 | One possible conformation |
| CH_3 \diagup CH_2 \diagup $\text{CH}-\text{CH}_2-\text{Br}$ | 653 | 622 | |
| CH_3 \diagup CH_2 \diagup $\text{CH}-\text{CH}_2-\text{CH}_2-\text{Br}$ | 650 | 568 | |
| CH_3 \diagup $(\text{CH}_2)_3-\text{C}-\text{Br}$ | 679 | 517 | One possible conformation |

$\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Br}$, there is a possibility of free rotation of the chain, as well as a possibility of an interaction between the halogen atom and the benzene ring [12]. Phenylethyl bromide absorbs at 544 cm^{-1} and 649 cm^{-1} and phenylpropyl bromide at 563 cm^{-1} and 652 cm^{-1} . Benzyl bromide has a single band at 550 cm^{-1} .


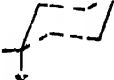
2. Halocycloalkanes

In cycloalkyl halides the halogen atom can be *axial* or *equatorial*. The two conformations have different C-hal frequencies. In Table II-66 are shown frequencies of the three monohalocyclohexanes [17].

In chlorocyclohexane in the liquid state, there is a dynamic equilibrium between conformations with an equatorial halogen and those with an axial

halogen atom due to the easy interconversion of the two forms. The two conformational isomers also coexist in the vapor phase. The infrared spectrum shows two bands. In the crystalline state the 688 cm^{-1} band disappears. This shows that in the crystalline state the molecule exists in a single conformation [18].

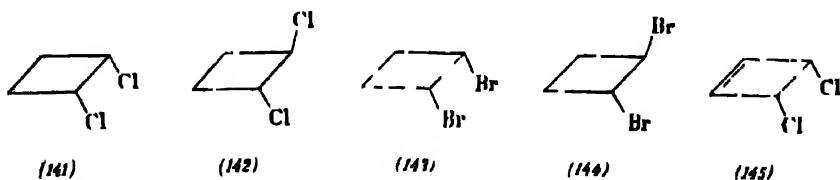
Table II-66 $\nu\text{C}-\text{X}$ frequencies (cm^{-1}) of halocyclohexanes in the liquid state

| | Equatorial bond | Axial bond |
|--------------|---|---|
| $\text{X} =$ |  |  |
| Cl | 742 | 688 |
| Br | 685 | 658 |
| I | 654 | 639 |

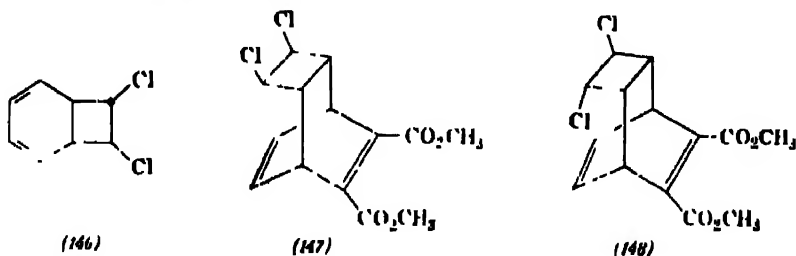
These remarks are confirmed by studies in the steroid series, where the conformations of C-Hal bonds have been established also by other means [19]. The fact that equatorial bonds have higher frequencies than axial ones is currently used in conformational analysis [19a; 19b]. Also, the intensity of bands is higher [17]. In 1, 2-dihalocyclohexanes [20], the two *cis* and *trans* stereoisomers can have either equatorial (e) or axial (a) halogen atoms.

The *cis* isomers can exist only in a single conformation, *a, e* [20, 21]. In the *trans* isomer, *a, a*, and *e, e* conformations are also possible. Spectroscopic studies of 1, 2-dichlorocyclohexane have shown that the *trans* isomer in solution or in the liquid state contains both isomers in dynamic equilibrium: $1a, 2a \rightleftharpoons 1e, 2e$. In the solid state there is a single conformation: $1e, 2e$.

cis-trans-Stereoisomers of 1, 2-dichlorobutane have $\nu\text{C}-\text{Cl}$ frequencies at 680 cm^{-1} (141) and 687 cm^{-1} (142), respectively (Fig. II-62a, b). *cis*-1, 2-Dibromocyclobutane (143) absorbs at 626 cm^{-1} and *trans*-1, 2-dibromocyclobutane (144), at 631 cm^{-1} [22].



In *cis*-3, 4-dichlorocyclobutene (145), the frequency of the $\nu\text{C}-\text{Cl}$ band is 603 cm^{-1} [23] (Fig. II-62c).



trans-7,8-Dichlorobicyclo [4.2.0] octadiene-2,4 (146) absorbs at 740 cm^{-1} [23, 21]. In adducts of isomeric *cis*- and *trans*-7,8 dichloro [4.2.0] octadiene-2,1

with acetylenedicarboxylic acid (147) and (148), C—Cl bands arise at 677 cm^{-1} and 645 cm^{-1} , respectively [23].

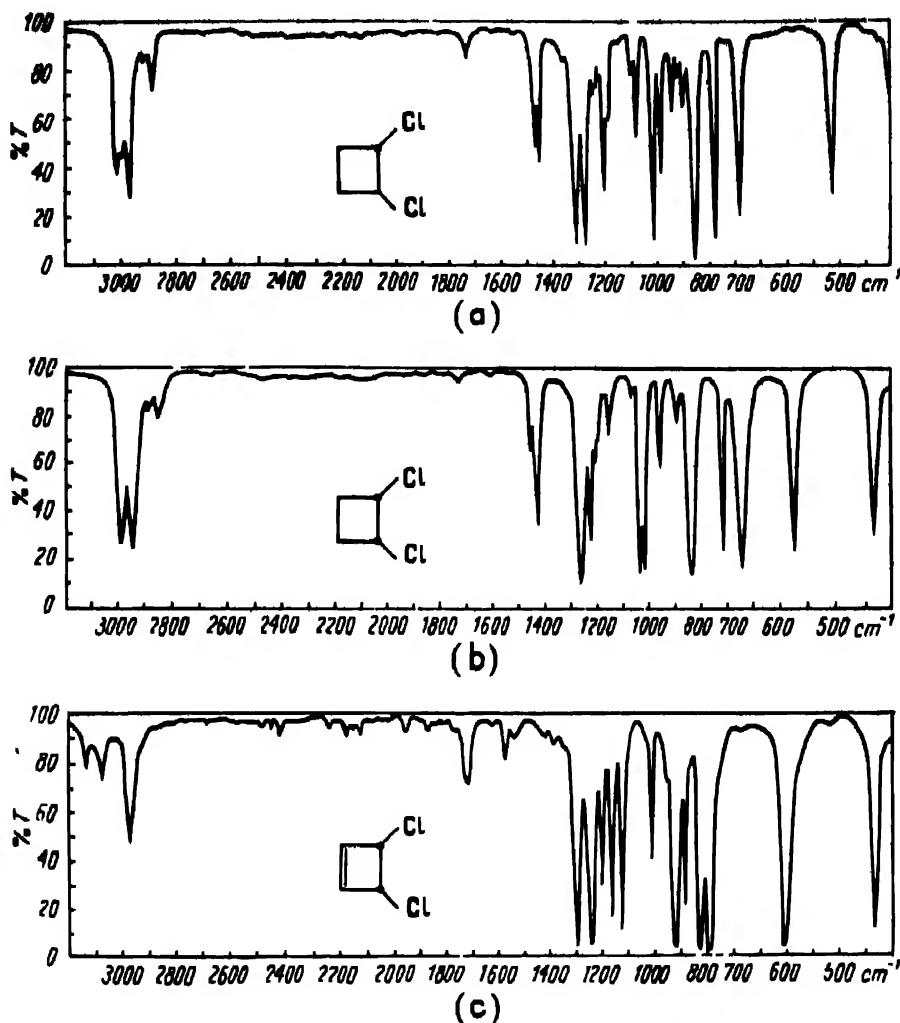


Fig. II-62 Infrared spectra of some dichlorocyclobutanes (liquid film): (a) *trans*-1,2-dichlorocyclobutane; (b) *cis*-1,2-dichlorocyclobutane; (c) *cis*-3,4-dichlorocyclobutane.

3. Unsaturated halides

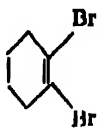
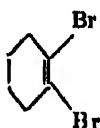
In unsaturated compounds with halogen atoms attached to one of the carbons of the double bond (vinyl halogen), the C—Hal frequencies are higher than in analogous saturated compounds (see Table II-67). In 1-chlorocyclohexene the $\nu_{\text{C—Cl}}$ frequency is 730 cm^{-1} and in 1-bromocyclohexene, 716 cm^{-1} [26]. In 1,2-dihalocyclohexenes both $\nu_{\text{C—X}}$ vibrations are active in the

Table II-67 $\nu\text{C}-\text{X}$ frequencies in vinyl halides [25]

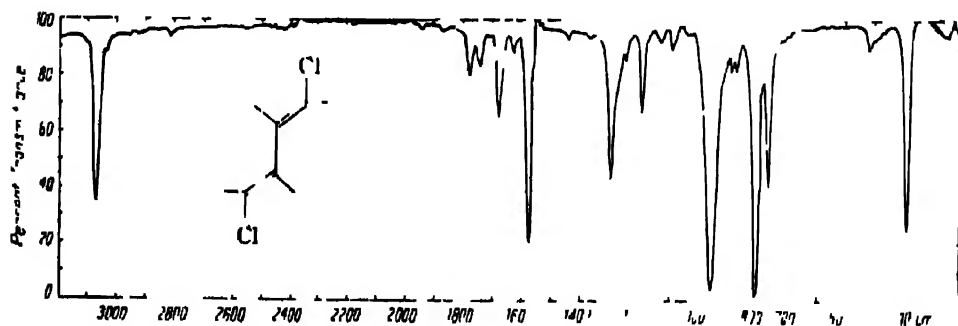
| Vinyl halide | C-X Frequencies, cm^{-1} | Ethyl halides | C-X Frequencies, cm^{-1} |
|-----------------------------------|--------------------------------------|-------------------------------------|--------------------------------------|
| $\text{CH}_2=\text{CH}-\text{Cl}$ | 724 | $\text{CH}_3-\text{CH}_2-\text{Cl}$ | 655 |
| $\text{CH}_2=\text{CH}-\text{Br}$ | 615 | $\text{CH}_3-\text{CH}_2-\text{Br}$ | 557 |
| $\text{CH}_2=\text{CH}-\text{I}$ | 535 | $\text{CH}_3-\text{CH}_2-\text{I}$ | 497 |

infrared. The asymmetrical stretching vibration has a higher frequency than the symmetrical one [26] (see Table II-68).

Table II-68 $\nu\text{C}-\text{X}$ frequencies (cm^{-1}) in dihalocyclohexenes [26]

| Compound | $\nu\text{C}-\text{X}$ asym | $\nu\text{C}-\text{X}$ sym |
|---|-----------------------------|----------------------------|
|  | 790 | 575 |
|  | 753 | 538 |

1, 4-Dichlorobutadiene (*trans-trans*) (149) has the two frequencies $\nu\text{C}=\text{C}$ at 760 cm^{-1} and 805 cm^{-1} (Fig. II-63) [23].

Fig. II-63 Infrared spectrum of 1,4 dichlorobutadiene (*trans trans*) (solution in CS_2 and CCl_4).

4. Di- and polyhalogenated compounds with several halogen atoms attached to the same carbon atom

In halides $>\text{CX}_2$ and $-\text{CX}_3$, the frequency of the $\text{C}-\text{X}$ vibration increases substantially as compared to monohalogenated analogs (see Table II-69) [27, 28].

CX_2 and CX_3 groups behave like CH_2 and CH_3 groups. They have stretching and deformation vibrations like those shown in Figs II-3 and II-4. Their identification is more difficult in the case of chloro- and bromo- derivatives because the corresponding stretching vibrations give rise to absorptions in a crowded region of the spectrum and the frequencies of the deformation modes are too low.

The first overtone of the $C-X$ vibration in polychloro-compounds arises in the region $1470-1500\text{ cm}^{-1}$.

C-H vibrations. C-H bands in CH_3 , CH_2 , and CH groups with carbon atoms attached to one, two, or three halogen atoms, respectively, are influenced by the $-I$ effect of the halogen atom. The asymmetrical stretching vibration of the CH_3 group occurs above 3000 cm^{-1} , reaching the $\nu C-H$ region of unsaturated and aromatic compounds. Shifts in the same direction are observed in the CH_2 group of dihalogenated compounds CH_2X_2 . The CH bond in CHX_2 has a frequency of $3030-3040\text{ cm}^{-1}$ (Table II-70) [29].

Table II-69 $\nu C-X$ frequencies (cm^{-1}) in halogenated compounds [28, 29]

| X | Type of compound | |
|----|------------------|-----------|
| | $+CX$ | $>CX_2$ |
| F | 1000-1120 | 1200-1350 |
| Cl | 570-625 | 710-780 |
| Br | 514-580 | 600-680 |
| I | 490-500 | — |

Table II-70 νCH frequencies in alkyl halides (cm^{-1})

| Frequency | F | Cl | Br | I |
|---------------|------|------|------|------|
| CH_3X sym | 2964 | 2966 | 2972 | 2970 |
| asym | 2982 | 3042 | 3056 | 3060 |
| CH_2X_2 sym | 2949 | 2985 | 2988 | 2967 |
| asym | 3012 | 3048 | 3065 | 3049 |
| CHX_2 | 3031 | 3040 | 3040 | — |

The shift increases with the atomic weight of the halogen atom and, for a given halogen, with the number of atoms attached to the same carbon (with the exception of some iodides).

The phenomenon is due to the $-I$ effect of the electronegative halogen atoms on the hybridization of the carbon atom. The orbitals of the $C-H$ bond become richer in s -component and the force constant (hence the frequency) increase accordingly.

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CHAPTER 3

HYDROXY COMPOUNDS (ALCOHOLS, PHENOLS) AND THEIR FUNCTIONAL DERIVATIVES

From the spectroscopic point of view hydroxy compounds can be regarded as derivatives of water, formed by substitution of a hydrogen atom with an organic radical.

The water molecule has three normal vibrational modes shown in Fig. I-36.

Modes ν_1 and ν_2 correspond approximately to the symmetrical (3652 cm^{-1}) and asymmetrical (3756 cm^{-1}) stretching modes of the O—H bonds. In principle ν_2 (1595 cm^{-1}) is a deformation mode of the angle H— $\hat{\text{O}}$ —H.

Hydroxy compounds R—OH show, by analogy with water, the frequencies of the functional group, perturbed by the vicinity of the organic radical. Consequently, the characteristic features in their spectra are stretching and deformation modes of O—H and C—O—H bonds.

The band corresponding to the stretching vibration of the O—H bond is one of the earliest known in infrared spectroscopy (1895) [1]. This band has been extensively studied both in the region of the fundamental vibration and in that of overtones, particularly in works concerned with inter- and intramolecular associations through hydrogen bonds.

The strongly electronegative oxygen atom attached through its two valencies to a hydrogen atom and a carbon from the organic group has two pairs of unshared electrons which enable the formation of hydrogen bonds between alcohol molecules, the same way as in water. Consequently, in the infrared spectrum, the band arising from the stretching vibration of the hydroxyl group in free alcohol disappears and a new band at lower frequencies appears instead, arising from the $\cdots\text{O}-\text{H}\cdots\text{O}$ bond in molecules of associated alcohol. The position and intensity of these two types of bands are essential elements in molecular structure studies.

The hydroxyl group in alcohols can form hydrogen bonds with other functional groups acting as donors or acceptors (see "Hydrogen bonds"). The vibration of the O—H bond, and particularly that of the C—O bond, is further influenced by the nature of the organic group.

The main changes in frequency arise from inductive (*I*) and conjugative (*E*) electronic effects of the group R. Mass and field effects result in much smaller variations in frequency. Consequently various classes of hydroxy derivatives can be differentiated by their infrared spectra: (a) saturated alcohols with the OH group attached to an alkyl or cycloalkyl radical and unsaturated or aromatic alcohols with the OH group attached to a saturated carbon atom of an alkene chain or a side chain of an aromatic hydrocarbon; (b) phenols, with the hydroxyl group attached to an aromatic ring; (c) enols, with the OH group attached to the carbon atom of a double bond. The large differences in frequency are partly because of conjugation of the unshared electrons of the OH group with π electrons of unsaturated and aromatic systems. This results in an increase of the C—O bond order and a simultaneous weakening of the O—H bond. Consequently, the force constant, hence the frequency, of the C—O bond increases and that of the O—H bond decreases.

In saturated alcohols, where the group R has only an inductive effect, shifts in frequency are associated with the nature of the carbon atom (primary, secondary, or tertiary) bearing the OH group.

1. Monohydroxy derivatives

a. **OH stretching vibration 1. Saturated alcohols.** The strong band observed in spectra of alcohols at $3500\text{--}3700\text{ cm}^{-1}$ was assigned to the stretching vibration of the O—H group. The large limits mentioned in the old literature are due to the low dispersion power of sodium chloride prisms used in early spectrometers. The use of lithium fluoride prisms enabled a more accurate assessment of the region characteristic for the stretching mode of the free OH bond ($3600\text{--}3650\text{ cm}^{-1}$). Because of its high intensity, the ν OH band can be differentiated readily from overtones and combinations arising in this region [1–5].

The assignment of the ν OH band is supported by the isotope effect. On deuteration, the absorption of the OH group at ca. 3600 cm^{-1} is replaced by that of the ν OD vibration, occurring in the $2400\text{--}2650\text{ cm}^{-1}$ region.

In the spectra of alcohols, the frequency of the free ν OH vibration is best measured in the vapor phase or in very dilute solution (below $0.005\text{ }m$) in nonpolar solvents (CCl_4 , CS_2). Because of the tendency of the OH group to form hydrogen bonds, the band arising from the free hydroxyl gradually disappears with increasing concentration and a broad band at lower frequency arising from the bonded hydroxyl appears instead. In polar solvents ν OH frequency measurements are prevented by the association of alcohol molecules with solvent molecules. Even in nonpolar solvents small frequency shifts are observed compared to spectra recorded in vapor phase. This is due, in part, to the formation of van der Waal's bonds with the solvent [1, 5].

In the series of saturated aliphatic alcohols, the first member, methanol, has the highest ν OH frequency (3642 cm^{-1}). Higher members have frequencies in the range $3640\text{--}3605\text{ cm}^{-1}$, decreasing in the order primary > secondary > tertiary [1, 6]; mean values are

| | |
|--------------------|--|
| primary alcohols | $-\text{CH}_2\text{OH } 3642\text{ cm}^{-1}$, |
| secondary alcohols | $>\text{CHOH } 3629\text{ cm}^{-1}$, |
| tertiary alcohols | $>\text{C.OH } 3618\text{ cm}^{-1}$. |

Band intensities decrease in the same order [7]. The decrease in frequency and intensity in the direction shown can be explained by the inductive effect (+I) of alkyl groups. Taking into account the possibility of partial overlap between bonded and free ν OH bands, we must use the above assignments cautiously in interpretative work [5].

2. **Hydrogen bonds between alcohol molecules.** In the liquid state, in concentrated solutions, or in the solid state, the free ν OH band in the $3600\text{--}3650\text{ cm}^{-1}$ region does not occur. Another band, much broader and much stronger is observed instead, at $3200\text{--}3400\text{ cm}^{-1}$ (Fig. II-64) [1, 5, 7a].

This suggested the idea that the bonded ν OH band is a composite of a large number of unresolved bands, corresponding to different modes of association of alcohol molecules. The band maximum depends on concentration,

nature of the solvent, temperature, etc. It was shown that depending on concentration, three types of bands can be identified. They are assigned to the free hydroxyl, to hydroxyl dimers, and to polymeric forms. For cyclohexanol, the following maxima were obtained at various concentrations [5]:

| | | | |
|--------|-------|-----------------------------|--|
| 0.01 m | | 3620 cm^{-1} | free νOH |
| 0.03 m | 3485, | 3620 cm^{-1} | νOH dimer, free νOH |
| 0.01 m | 3360, | 3485, 3620 cm^{-1} | νOH polymer νOH dimer, free νOH |
| 0.2 m | 3350, | 3620 cm^{-1} | νOH polymer, νOH free |
| 1.0 m | 3320, | 3615 cm^{-1} | νOH polymer, νOH free |

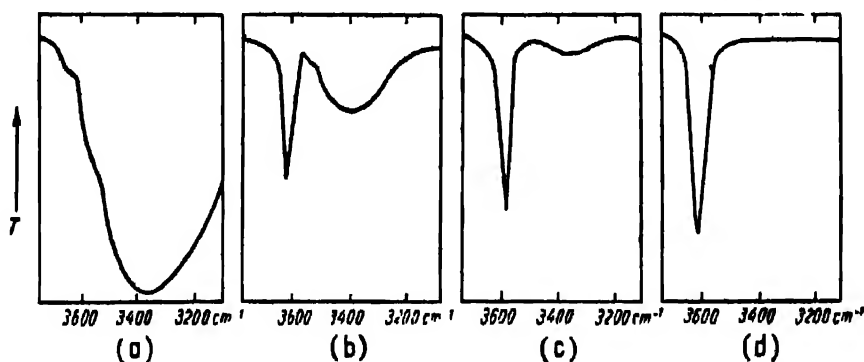
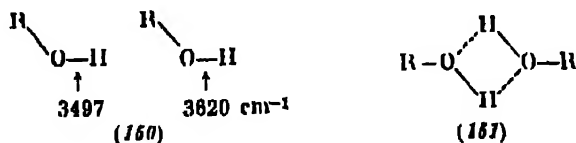
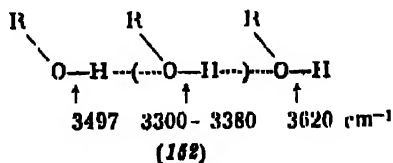


Fig. 11-64 Hydrogen bonds in 1-phenylcyclobutanol:
(a) liquid film; (b) 0.07m solution in CCl_4 ; (c) 0.05m solution in CCl_4 ; (d) 0.03m solution in CCl_4 .

In solutions in which dimers predominate, besides the free νOH band, another band at ca. 3620 cm^{-1} is sometimes observed; it is assigned to the vibration of the terminal hydroxyl (150). Also, the bonded νOH band (3497 cm^{-1}) can be split into a doublet because of the contribution of the cyclic dimeric form (151) [5].

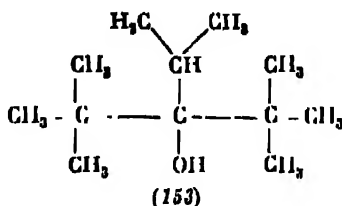


The polymeric form (152) has a strong band at $3300-3380 \text{ cm}^{-1}$. In this association mode, both the oxygen and the hydrogen atoms participate in hydrogen bonding.



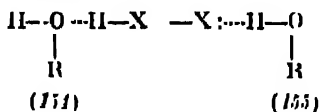
Hydrogen bonds between alcohol molecules are formed and broken continuously. Consequently, the number of molecules in these aggregates varies with the nature of the alcohol, temperature etc. In fact, the band represents the frequency of many linkages of various types. In thin films obtained by rapid cooling of molten solid alcohols, ν OH frequencies are closer in value to those in concentrated solutions than in crystals. This shows that in the crystalline state the orientation of the molecule is such as to form the strongest hydrogen bonds [1]. The exact interpretation of the polymeric association of hydroxyl groups has been discussed in a number of theoretical studies.

In alcohols branched in the α -position, where association is impossible by virtue of steric hindrance, the spectrum shows only the free ν OH frequency [8], for example compound (153) shows a single band of the monomeric alcohol.



The ν OH band can be used to establish the proportion of free hydroxyl groups [1]. By measuring the relative intensity of associated and free OH bands at various concentrations, it is possible to determine the dissociation constant of polymeric alcohols [9, 9a].

3. *Hydrogen bonds between the OH group and other functional groups.* The OH group in alcohols can form hydrogen bonds with molecules of donors (154) and acceptors of protons (155).



Acceptors may be groups with unshared electrons, such as $\text{C}=\text{O}$, COOR , COOH , OR , NR_2 , halogen [9b-9h] (see below). It has also been shown that hydrogen bonds can be formed by means of π electrons of double bonds, triple bonds, and aromatic rings.

Table II-71 shows associated and free ν OH frequencies for a number of primary alcohols, $\text{R}-\text{CH}_2\text{OH}$, where the OH group is separated from the acceptor by one, two, or three CH_2 groups [10]. A similar interaction takes place with the three-membered ring.

It can be seen that relative to the intensity of the free ν OH band, the intensity of the associated band falls with increasing number of CH_2 groups. At the same time, $\Delta\nu$ has greater values, which means that the hydrogen bond becomes stronger.

If the OH group belongs to a rigid system, the position of associated and free ν OH bands can give information on the orientation of the OH group with respect to the double bond or the functional group of the acceptor [10]. In

endo-8-hydroxytricyclo [5.2.1.0]^{2,6} decone-4 (156), the frequency of free νOH is 3624 cm^{-1} and the frequency of associated νOH is 3575 cm^{-1} .

The distance between the bands ($\Delta\nu=49\text{ cm}^{-1}$) reflects the strength of the hydrogen bond formed between the OH group in the 8 position and the

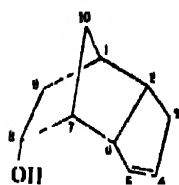
Table II-71 Frequencies of hydrogen bonds in systems O—H... π (electrons) [10]

| Alcohol | $\nu\text{OH free, cm}^{-1}$ | $\nu\text{OH assoc., cm}^{-1}$ | $\Delta\nu, \text{cm}^{-1}$ |
|--|------------------------------|--------------------------------|-----------------------------|
| <i>Alcohols with double bonds</i> | | | |
| $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$ | 3631* | 3618 | 13 |
| $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2\text{OH}$ | 3634 | 3594 | 40 |
| $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH}$ | 3637 | - | - |
| <i>Alcohols with triple bonds</i> | | | |
| $\text{CH}\equiv\text{C}-\text{CH}_2\text{OH}$ | - | 3620 | 11-18 |
| $\text{CH}\equiv\text{C}-\text{CH}_2-\text{CH}_2\text{OH}$ | 3640 | 3598 | 42 |
| $\text{CH}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH}$ | 3638 | 3588 | 50 |
| <i>Aromatic alcohols</i> | | | |
| $\text{C}_6\text{H}_5-\text{CH}_2\text{OH}$ | 3632* | 3615 | 17 |
| $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2\text{OH}$ | 3634 | 3606 | 28 |
| $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{OH}$ | 3638 | - | - |
| <i>Cyclopropylcarbinol</i> | | | |
| $\triangleright\text{CH}_2\text{OH}$ | 3631* | 3615 | 16 |

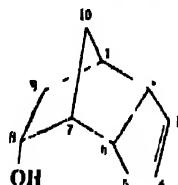
* Overlapped

double bond in the 4 position. The smaller value of $\Delta\nu$ ($3622-3591=31\text{ cm}^{-1}$) in isomer (156b) shows the formation of a weaker hydrogen bond in agreement with the larger distance between the OH group (8 position) and the double bond (3 position). In molecules with a norbornene skeleton (157a) and (157b), only the *endo* isomers can form a hydrogen bond. In *endo*-2-norbornenol-5 (157a), the free νOH vibration has a frequency of 3622 cm^{-1} and the associated νOH of 3592 cm^{-1} ($\Delta\nu=30\text{ cm}^{-1}$). 5-*endo*-Methyl-2-norbornene-5-*exo*-ol (157b), absorbs only at 3610 cm^{-1} (free νOH) [10].

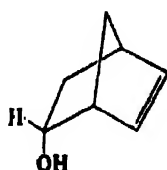
cis and *trans* Isomers of 1, 2-diphenyl-3, 4-dihydroxycyclobutene can be distinguished by their absorption in the νOH region [11]. The *cis* isomer (158a) has two bands in this region. The 3602 cm^{-1} band is assigned to the



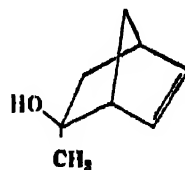
(156a)



(156b)

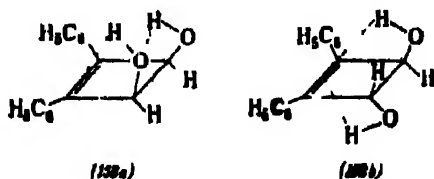


(157a)



(157b)

O—H... π bond and the 3557 cm^{-1} band to the O—H ... O bond. The *trans* isomer (158b) has a single absorption at 3602 cm^{-1} .



The capacity of the benzene ring to act as an electron donor has been demonstrated in several ways [12]. In the infrared the benzenemethanol interaction was first studied in the overtone region. The results obtained in the fundamental νOH region on the interaction of CH_3OD with various monocyclic aromatic hydrocarbons are shown in Table II-72.

Table II-72 νOD frequencies of CH_3OD in the presence of aromatic compounds [13]

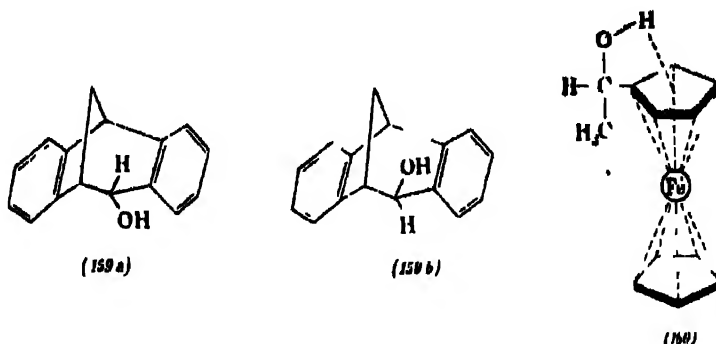
| (H_2O with: | $\nu\text{OD}, \text{cm}^{-1}$ | $\Delta\nu$ compared with CH_3OD in $\text{CCl}_4, \text{cm}^{-1}$ |
|------------------------------|--------------------------------|--|
| Carbon tetrachloride | 2689 | — |
| Benzene | 2665 | 24 |
| Toluene | 2663 | 26 |
| <i>o</i> -Xylene | 2659 | 30 |
| <i>m</i> -Xylene | 2660 | 29 |
| Mesitylene | 2655 | 34 |
| Chlorobenzene | 2668 | 21 |
| Bromobenzene | 2669 | 20 |
| <i>o</i> -Dichlorobenzene | 2676 | 13 |

The $\Delta\nu$ values show that the basicity, i.e., the capacity to donate electrons decreases in the order: mesitylene > xylene > toluene > benzene > chlorobenzene > *o*-dichlorobenzene.

The νOH frequency of *endo*-2, 3, 6, 7-dibenzobicyclo [3. 2. 1] octa-2, 6-dieneol-4 (159a) is 33 cm^{-1} lower than that of the *exo* isomer (159b) because of the interaction of the OH group with the adjacent benzene ring [14].

The presence of an intramolecular hydrogen bond between the aromatic ferrocene ring and the OH substituent was demonstrated in a rather interesting way [15]. α -Hydroxyethylferrocene (160) in carbon tetrachloride solution shows a band at 3617 cm^{-1} (free νOH) and a strong band, independent of concentration, but temperature dependent, at 3574 cm^{-1} (assigned to the OH group hydrogen bonded to the ferrocene ring) ($\Delta\nu = 43 \text{ cm}^{-1}$). In a mixture of 0.1 mole *n*-butanol and ferrocene in CCl_4 , the frequency νOH assoc. is

3597 cm^{-1} [15]. The aromatic analog β -phenylethanol $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$ absorbs at 3630 cm^{-1} (free νOH) and at 3601 cm^{-1} (νOH associated with the benzene ring) ($\Delta \nu = 29 \text{ cm}^{-1}$). Consequently, the ferrocene ring forms stronger hydrogen bonds than the benzene ring.



4. The νOH vibration in conformational analysis of cycloalkanol. It has been shown that in cyclohexanols and in alcohols of the terpene series it is possible to distinguish between primary, secondary (axial or equatorial) and tertiary (axial or equatorial) OH groups by studying the νOH absorption [16, 17]. In cyclohexane derivatives the primary hydroxyl in the hydroxymethylene chain has the highest frequency (in *cis*-2-methylcyclohexylmethanol it occurs at 3640 cm^{-1} and in the *trans* isomer, at 3641 cm^{-1}) [18]. The secondary hydroxyl group in the cyclohexane ring (axial or equatorial) has a frequency ranging from 3622–3632 cm^{-1} . The lowest frequency (3619 cm^{-1}) occurs in the tertiary hydroxyl group (Table II-73). The frequency of an

Table II-73 νOH frequencies (cm^{-1}) in alkylcyclohexanols

| Compound | Free νOH (solution in CCl_4) [18] | OH Conforma- tion | νOH (solution in CS_2) [16] | |
|--|---|-------------------------|---|------------|
| | | | free | associated |
| <i>cis</i> -2-Methylcyclohexanol | 3632 | <i>a</i> | 3650 | 3520 |
| <i>trans</i> -2-Methylcyclohexanol | 3622 | <i>e</i> | 3613 | 3400 |
| <i>cis</i> -3-Methylcyclohexanol | 3622 | <i>e</i> | 3610 | 3380 |
| <i>trans</i> -3-Methylcyclohexanol | 3627 | <i>a</i> | 3650 | 3400 |
| <i>cis</i> -4-Methylcyclohexanol | 3628 | <i>a</i> | — | — |
| <i>trans</i> -4-Methylcyclohexanol | 3623 | <i>e</i> | — | — |
| Isomenthol | 3627 | <i>e</i> | — | — |
| Menthol | 3628 | <i>e</i> | — | — |
| Neomenthol | 3632 | <i>a</i> | 3622 | 3510 |
| Neoisomenthol | 3632 | <i>a</i> | 3635 | 3520 |
| <i>cis</i> -2-Methylcyclohexylmethanol | 3640 | primary | — | — |
| <i>trans</i> -2-Methylcyclohexylmethanol | 3641 | primary | — | — |
| <i>trans</i> - <i>p</i> -Menthane-4-ol | 3619 | tertiary | — | — |

axial hydroxyl group is higher than that of an equatorial OH [18]. This was explained by the repulsion between atoms in 1,3-axial positions of the cyclohexane ring, hindering the vibration of the oxygen atom responsible for the increase in force constant of the O—H bond. In equatorial OH groups the motions are less restrained (Fig. II-65).

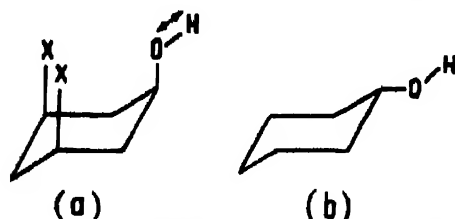


Fig. II-65 (a) Axial and (b) equatorial position of the OH group in cyclohexanol.

The small, but significant, differences between the frequencies of axial and equatorial hydroxyl groups are of value in establishing the conformation of substituents in some mono- and dialkylcyclohexanols, where substituents compete for the thermodynamically more favored equatorial position (c) [17, 18].

In a number of *cis*- and *trans*-monoalkylcyclohexanols substituted in the 2-3-, and 4-positions with methyl, isopropyl, and *t*-butyl groups, the limits for axial and equatorial ν OH absorptions were set at 3627–3632 cm^{-1} and 3622–3623 cm^{-1} , respectively. For triterpenes the limits are 3637–3669 cm^{-1} and 3629–3630 cm^{-1} , respectively [19].

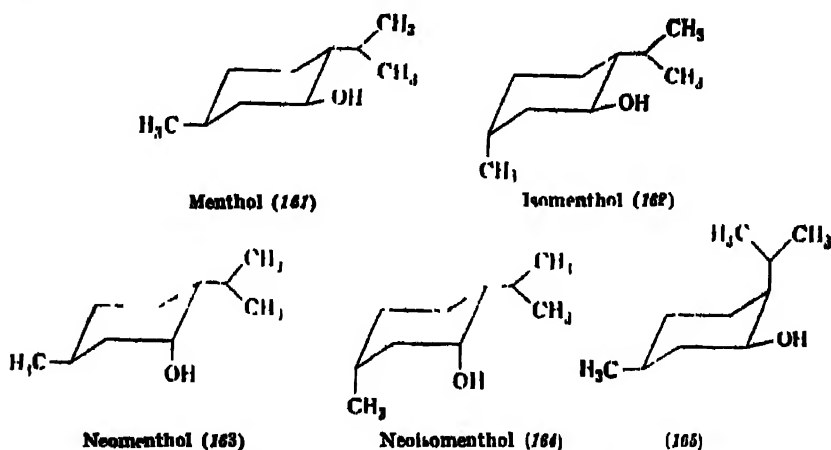
The conformation of the hydroxyl group, established by means of these frequencies, is shown in Table II-73 [18].

Table II-73 shows that in the case of methylcyclohexanols the conformation with axial OH (ν OH frequency 3627–3632 cm^{-1}) is predominant in *cis*-2-methyl and *cis*-4-methyl derivatives. The *trans* isomers, with equatorial OH have frequencies in the range 3622–3623 cm^{-1} [20]. In the last two columns of Table II-73 are shown free and associated ν OH frequencies in CS_2 solutions [16]. Similar assignments were made for a number of *cis* and *trans* alkyl-2-, 3-, or 4-cyclohexanols (methyl, isopropyl, *t*-butyl) [16]. However, no general rule can be established: for example in *cis*- and *trans*-cyclohexylcyclohexanols, the difference in frequency is insignificant, and in decalols there is no agreement whatsoever [16]. In dialkylcyclohexanols a small increase in frequency is observed, assigned to the increased rigidity of the system due to the presence of an additional alkyl group. Based on criteria for monoalkylcyclohexanols, the frequency of 3628 cm^{-1} in menthol was assigned (161) to the tri-equatorial conformation [16–18]. The frequency in isomenthol (3627 cm^{-1}) supports structure (162) where the OH and isopropyl groups are equatorial and the CH_3 group axial.

In neomenthol and neoisomenthol the isopropyl, methyl, and hydroxyl groups compete for the equatorial positions. In neomenthol the absorption at 3632 cm^{-1} shows that the OH group is axial; consequently, the methyl and isopropyl groups must be equatorial (163).

In neoisomenthol the choice has to be made between the two conformations (164) and (165) with the isopropyl group equatorial (164) or with two equatorial groups (OH and CH_3) and the isopropyl group axial (165). The absorption at 3632 cm^{-1} (ν OH axial) in neoisomenthol supports the predo-

minant conformation (164) [18]. Subsequently it was shown that dialkylcyclohexanols are conformationally heterogeneous, having characteristic C—O frequencies for both axial and equatorial OH bonds [16].



In triterpene alcohols with cyclohexane rings, the frequencies of the O—H group are higher than in monocyclic compounds [20]. Also, in this case the ν O—H frequencies enable one to distinguish between the axial and equatorial orientation of the functional group (Table II-74).

In various members $\Delta \nu$ OH (free ν OH — associated ν OH) varies between 100 and 300 cm^{-1} .

The intensity of the associated hydroxyl band is lower for axial than for equatorial OH. The conclusion was drawn that axial hydroxyl groups associate less readily than equatorial ones [16]. The increase in volume of the substituent adjacent to the OH group reduces the possibilities of association.

A study of α -indanol has shown that the associated hydroxyl band occurs in the racemic form at 3230 cm^{-1} and in the dextrorotatory enantiomer at 3320 cm^{-1} . The phenomenon was explained by a different mode of association of the two types of molecules [21].

b. **C—OH stretching vibration.** The strong absorption observed in spectra of hydroxy derivatives between 1000 and 1250 cm^{-1} was assigned to a characteristic vibration of the C—OH group. The exact origin of this band which undoubtedly involves hydrogen participation is not known. Consequently, the notation ν C—OH is considered to be more correct than ν C—O. Early studies of this region have already shown a correspondence between the frequency of this vibration and the nature of the hydroxyl group. This allows the

Table II-74 Characteristic ν OH frequencies in triterpene alcohols (solution in CCl_4) [19, 20]

| Hydroxyl group | ν OH, cm^{-1} |
|--|----------------------------|
| Primary | 3640—3641 |
| Secondary axial | 3635—3638 |
| Secondary equatorial (C_p) | 3628—3630 |
| Secondary equatorial (C_{11}) | 3623—3625 |
| Tertiary axial | 3617—3619 |
| Tertiary equatorial | 3613 |

possibility to differentiate various alcohols by their absorption in the 1000–1200 cm^{-1} region [22–24]. It was stated that primary alcohols absorb at ca. 1050 cm^{-1} , secondary alcohols at 1100 cm^{-1} and tertiary alcohols at 1150 cm^{-1} . These findings were confirmed by subsequent studies [25, 26] of saturated aliphatic alcohols with chains up to 12 carbon atoms.

More recent systematic studies of a large number of various alcohols have shown that a clear distinction between the three types of compounds cannot be made simply by assigning the absorption bands to one of the zones mentioned above. The C–O bond is especially sensitive to electronic and symmetry effects resulting in changes in force constants, hence in band positions. It becomes increasingly difficult to make accurate assignments when molecular symmetry and structural elements in the vicinity of the C–O group can by their nature have a strong influence on the vibration of the bond. It has been shown that the occurrence of a band between 1205 and 1125 cm^{-1} may indicate the presence of a saturated tertiary aliphatic alcohol or of a highly symmetrical secondary alcohol. An absorption between 1085 and 1125 cm^{-1} very probably belongs to a saturated aliphatic secondary alcohol, to a cyclic tertiary alcohol, or to an α , β -unsaturated alcohol. If the band occurs between 1085 and 1100 cm^{-1} , it is very likely that a secondary alcohol branched in the α -position is involved. A band between 1050 and 1085 cm^{-1} may arise from an unsaturated secondary alcohol, a primary straight chain aliphatic alcohol, or a secondary five- or six-membered cyclic alcohol. Seven- and eight-membered cyclic secondary alcohols absorb at ca. 1050 cm^{-1} [27]. Thus the distinctions are not clear-cut and for structure determinations additional proof from other regions of the spectrum or by different means (physical or chemical) are necessary.

1. *Primary alcohols.* In straight chain primary aliphatic alcohols (Table II-75), the C–O vibration frequency occurs in the range 1030–1075 cm^{-1} .

Table II-75 Acyclic primary alcohols
[27]

| Alcohol | $\nu_{\text{C-OH}}$, cm^{-1} |
|-------------------------|--|
| Methanol | 1030 |
| Ethanol | 1050 |
| <i>n</i> -Propanol | 1060 |
| <i>n</i> -Butanol | 1075 |
| <i>n</i> -Pentanol | 1060 |
| <i>n</i> -Hexanol | 1060 |
| <i>n</i> -Heptanol | 1060 |
| <i>n</i> -Octanol | 1060 |
| 2-Methylbutanol-1 | 1040 |
| 3-Methylbutanol-1 | 1060 |
| 2, 2-Dimethylpropanol-1 | 1030 |

Chain branching in the α -position lowers the frequency by ca. 15 cm^{-1} , i.e. the C–OH frequency of the unbranched alcohol. Branching in the β -position does not have an analogous effect [27].

Band intensity decreases with increasing chain length (increasing ratio between the hydrocarbon chain and the OH group).

2. *Secondary alcohols.* In straight chain saturated secondary alcohols, the $\nu_{\text{C-OH}}$ frequency, occurs at $1100 \pm 5 \text{ cm}^{-1}$. In compounds $\text{CH}_3\text{—CHOH—R'}$ and $\text{C}_2\text{H}_5\text{—CHOH—R'}$, lengthening of the chain R' results in a very small

shift of the band towards higher frequencies. In secondary alcohols R—CHOH—R' the increase in frequency is small when chains R and R' become longer [27] (Table II-76).

Branching in an α -position results in a decrease in $\nu\text{C}-\text{OH}$ frequency by ca. 15 cm^{-1} , cf. the frequency of the straight chain isomer. Lengthening of the branched chain does not seem to have any influence on the vibration. Branching at both carbon atoms in α -positions appears to have an opposite effect (Table II-77).

Table II-76 $\nu\text{C}-\text{OH}$ frequencies in acyclic secondary alcohols $\text{R}-\text{CHOH}-\text{R}'$ [27]

| R | R' | $\nu\text{C}-\text{OH}, \text{cm}^{-1}$ | R | R' | $\nu\text{C}-\text{OH}, \text{cm}^{-1}$ |
|--------|----------|---|----------|----------|---|
| Methyl | Methyl | 1105 | Ethyl | n-Butyl | 1108 |
| Methyl | Ethyl | 1105 | Ethyl | n-Hexyl | 1111 |
| Methyl | n-Propyl | 1106 | n-Propyl | n-Propyl | 1115 |
| Methyl | n-Butyl | 1106 | n-Propyl | n-Butyl | 1116 |
| Methyl | n-Hexyl | 1109 | n-Propyl | n-Hexyl | 1118 |
| Methyl | n-Nonyl | 1111 | n-Butyl | n-Butyl | 1115 |
| Ethyl | Ethyl | 1166 | n-Pentyl | n-Pentyl | 1119 |

3. *Cyclic secondary alcohols.* The $\nu\text{C}-\text{OH}$ absorption in cyclic secondary alcohols is shifted by $10-85\text{ cm}^{-1}$ toward lower frequencies, cf. acyclic compounds (1110 cm^{-1}) (see Table II-78). According to this criterion, cyclopro-

Table II-77 $\nu\text{C}-\text{OH}$ frequencies in branched acyclic secondary alcohols ($\text{R}-\text{CHOH}-\text{R}'$) [27]

| R | R' | $\nu\text{C}-\text{OH}, \text{cm}^{-1}$ |
|----------|----------|---|
| Methyl | i-Propyl | 1090 |
| Methyl | i-Butyl | 1109 |
| Methyl | t-Butyl | 1093 |
| Methyl | i-Hexyl | 1110 |
| i-Propyl | i-Propyl | 1098 |
| i-Butyl | i-Butyl | 1126 |
| t-Butyl | t-Butyl | 1163 |

Table II-78 $\nu\text{C}-\text{OH}$ frequencies in cyclic secondary alcohols [27]

| Alcohol | $\nu\text{C}-\text{OH}, \text{cm}^{-1}$ |
|---------------|---|
| Cyclopropanol | 1205 |
| Cyclobutanol | 1090 |
| Cyclopentanol | 1067 |
| Cyclohexanol | 1064 |
| (-)-Menthol | 1039 |
| Cycloheptanol | 1025 |
| Cyclooctanol | 1047 |

panol (1205 cm^{-1}) has an abnormal behavior, whereas cyclobutanol (1090 cm^{-1}) has an almost normal behavior. It appears more reasonable to compare cyclic alcohols with each other. Taking for reference the frequency 1067 cm^{-1} in cyclopentanol and 1064 cm^{-1} in cyclohexanol, the shift toward higher frequencies in strained rings becomes evident (in cyclobutanol the frequency is 1090 cm^{-1} and in cyclopropane, 1205 cm^{-1}). The frequency falls in cycloheptanol (1025 cm^{-1}) and tends toward normal values in the eight-membered ring. The increase in $\nu\text{C}-\text{OH}$ frequency in small rings is in line with the different nature of their bonds (see *cycloalkanes*). It is due to the increase in force constant, as a result of enrichment in s-component of the "special" small ring bonds. In the extreme case of cyclopropane bonds, the frequency shifts all the way to 1205 cm^{-1} , the calculated value for a hypothetical vinyl alcohol with the hydroxyl group attached to a sp^2 hybridized carbon atom ($=\text{C}-\text{OH}$).

In compounds with cyclohexane rings, the $\nu\text{C}-\text{OH}$ frequency varies with the axial or equatorial orientation of the hydroxyl group. The investigation of this region was of great value in conformational analysis work (see below).

4. *Tertiary alcohols.* In straight chain aliphatic tertiary alcohols with up to 17 carbon atoms, the $\nu\text{C}-\text{OH}$ frequency occurs at 1140 cm^{-1} [23]. However, the band position varies with the nature of the alcohol [27] (Table II-79), for example, *tert*-butanol absorbs at 1205 cm^{-1} . Chain branching in an α -position results in small shifts toward lower frequencies. The same

Table II-79 $\nu\text{C}-\text{OH}$ frequencies in tertiary alcohols $\text{R}_1\text{R}_2\text{R}_3\text{C}-\text{OH}$ [27]

| R_1 | R_2 | R_3 | $\nu\text{C}-\text{OH},$ cm^{-1} |
|---|---|--|--|
| CH_3 | CH_3 | CH_3 | 1205 |
| CH_3 | C_2H_5 | $\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5$ | 1142 |
| CH_3 | C_2H_5 | C_2H_5 | 1100 |
| C_2H_5 | C_2H_5 | C_2H_5 | 1009 |
| $\text{CH}_3-\text{O}-\text{C}_6\text{H}_4$ | $\text{CH}_3-\text{O}-\text{C}_6\text{H}_4$ | $\text{CH}_3-\text{O}-\text{C}_6\text{H}_4$ | 1020 |

effect is observed in cyclic tertiary alcohols; for example, 1-methylcyclohexanol-1 absorbs at 1117 cm^{-1} . Variations in frequency can be assigned to vibrational interactions between C-C and C-O bonds, which are stronger in this kind of structure.

It should be pointed out that triphenyl- and trianisylcarbinol absorb at about the same frequency as diphenylcarbinol.

5. *Unsaturated and aromatic alcohols.* The frequencies of secondary alcohols $\text{C}_6\text{H}_5-\text{CHOH}-\text{R}'$, where R' is a phenyl, β -naphthyl, or unsaturated group with a C=C double bond, are $30-50\text{ cm}^{-1}$ lower than in secondary aliphatic alcohols with similar structures [27], (Table II-80). The cyclopropane ring has

Table II-80 $\nu\text{C}-\text{OH}$ frequencies in unsaturated and aromatic alcohols $\text{R}-\text{C}(\text{OH})-\text{R}'$ [27]

| R | R | $\nu\text{C}-\text{OH},$ cm^{-1} | R | R' | $\nu\text{C}-\text{OH},$ cm^{-1} |
|------------|-------------|--|------------|------------------|--|
| Methyl | Phenyl | 1073 | Phenyl | <i>t</i> -Propyl | 1020 |
| Methyl | Cyclopropyl | 1076 | Phenyl | <i>t</i> -Butyl | 1000 |
| Butyl | Vinyl | 1060 | Phenyl | Phenyl | 1014 |
| Phenyl | Ethyl | 1039 | Phenyl | <i>p</i> -Tolyl | 1012 |

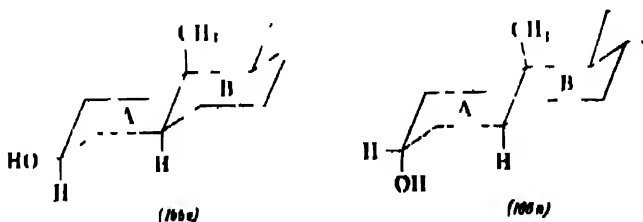
an analogous effect. In alcohols $\text{C}_6\text{H}_5-\text{CHOH}-\text{R}'$, where R' is an alkyl radical (methyl, *i*-propyl, *t*-butyl, cyclohexyl) the decrease in frequency is $85-100\text{ cm}^{-1}$. Similarly, a large decrease in frequency is observed in the case of two phenyl or two tolyl groups.

Consequently, unsaturation in the α -position results in a large decrease in frequency, and the $\nu\text{C}-\text{OH}$ band shifts to the region of primary alcohol absorptions.

Compared with aliphatic series, differences in frequency between primary, secondary, and tertiary aromatic alcohols are smaller.

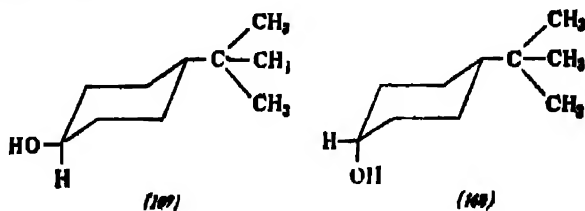
| | | |
|---|--|---|
| $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ 1010 cm^{-1} | $(\text{C}_6\text{H}_5)_2\text{CHOH}$ 1014 cm^{-1} | $(\text{C}_6\text{H}_5)_3\text{COH}$ 1009 cm^{-1} |
| CH_3OH 1035 cm^{-1} | $(\text{CH}_3)_2\text{CHOH}$ 1105 cm^{-1} | $(\text{CH}_3)_3\text{COH}$ 1205 cm^{-1} |

6. The $\nu\text{C}-\text{OH}$ vibration in conformational analysis of cycloalkanols. Infrared studies of a number of 3-hydroxy steroids have shown that the frequency of the $\nu\text{C}-\text{OH}$ vibration depends on the conformation of the OH group in the 3-position [28]. In compounds with the OH group in the equatorial position (166e), the C—O bond frequency is much higher than in isomers with axial OH groups (166a). In 3-hydroxy steroids with A/B rings *trans* and an equatorial 3β -hydroxyl, the $\nu\text{C}-\text{OH}$ frequency lies in the range 1037–1040 cm^{-1} ; whereas in compounds with A/B rings *trans* and an axial 3α -OH, the frequency is 996–1002 cm^{-1} [28]. Similar results were observed in other 2-, 3-, or 4-hydroxy steroids [29, 30].

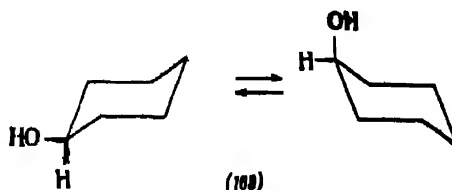


In triterpenes the frequency of the axial C—OH bond (1063–1069 cm^{-1}) is higher than that of the equatorial bond (1025–1040 cm^{-1}) [19]. In structural determinations this inversion has to be taken into account.

The use of the $\nu\text{C}-\text{OH}$ vibration was extended to the conformational analysis of simple cycloalkanols with various ring sizes. For cyclohexane derivatives, the two stereoisomers of 4-*t*-butylcyclohexanol were chosen as reference. The *t*-butyl group makes the ring rigid enough to stabilize the molecule in a single conformation [31, 32]. In the *trans* form (167), the two substituents are *equatorial*. In the *cis* form (168), the *t*-butyl group is *equatorial* and the OH group is *axial* [33].



cis-4-*t*-Butylcyclohexanol absorbs at 955 cm^{-1} , and *trans*-5-butylcyclohexanol, at 1062 cm^{-1} . By comparing the intensity of the 1069 cm^{-1} absorption in cyclohexanol (169) with that at 1062 cm^{-1} in *trans*-4-*t*-butylcyclohexanol, it was appreciated that cyclohexanol exists to the extent of 62–66% in equatorial conformation [33] (Fig. II-66).



$\nu\text{C}-\text{OH}$ frequencies in the $940\text{--}1070\text{ cm}^{-1}$ region were used to assign axial or equatorial conformations to substituents in a number of alkyl and

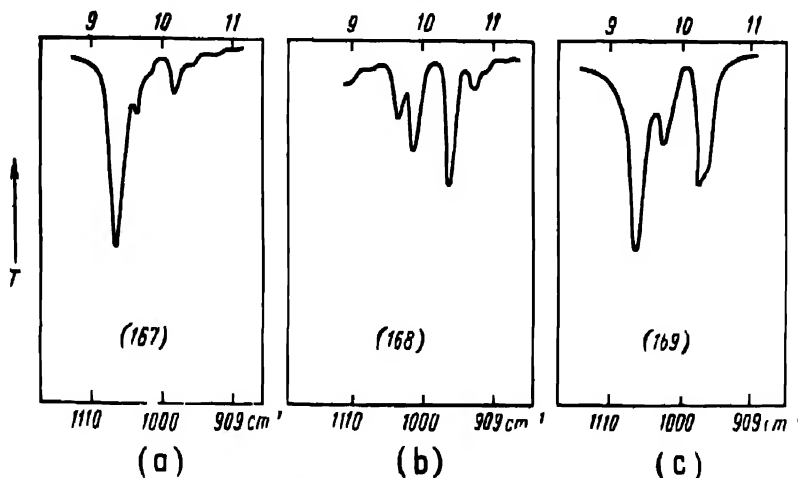


Fig. II-66 Stretching vibrations of axial and equatorial C—OH bonds in cyclohexanols:

(a) *trans*-4-*t*-butylcyclohexanol (OH equatorial); (b) *cis*-4-*t*-butylcyclohexanol (OH axial); and (c) cyclohexanol.

dialkylcyclohexanols and some α - and β -decanols [16]. The frequencies of some characteristic representatives of *cis* and *trans* 2-, 3-, or 4-alkylcyclohexanols, where the alkyl group is methyl, ethyl, isopropyl, or *t*-butyl, are shown in Table II-81.

These frequencies show that monoalkyl derivatives are conformationally homogeneous. In *trans*-2-alkyl isomers, the hydroxyl is equatorial and in *cis*-2-alkyl derivatives it is axial. In 3-alkylcyclohexanols *cis* isomers have equatorial OH, and *trans* isomers have axial OH [16].

With few exceptions polyalkylcyclohexanols are conformationally heterogeneous [16] (see νOH vibration). Menthol is an exception, its OH group being exclusively equatorial.

Table II-51 $\nu\text{C}-\text{OH}$ frequencies (cm^{-1}) in monosubstituted cyclohexanols [15]

| Substituent | $\nu\text{C}-\text{OH}$ | | | |
|----------------------------------|-------------------------|----------------|------------|----------------|
| | Equatorial | | Axial | |
| | Main band | Secondary band | Main band | Secondary band |
| <i>cis</i> -2-Methyl | 1065 | 956 | * 975 | 1025 1014 |
| <i>trans</i> -2-Methyl | 1042 | 980 | — | — |
| <i>cis</i> -3-Methyl | 1048 1019 | 972 | — | — |
| <i>trans</i> -3-Methyl | — | — | 994 943 | 1032 |
| <i>cis</i> -2-Ethyl | — | — | 965 | 1023 |
| <i>trans</i> -2-Ethyl | 1064 | 987 | — | — |
| <i>cis</i> -2-Isopropyl | — | — | 968 | 1000 |
| <i>trans</i> -2-Isopropyl | 1047 | 995 | — | — |
| <i>cis</i> -3-Isopropyl | 1045 | 980 | — | — |
| <i>trans</i> -3-Isopropyl | — | — | 977 | 1045 |
| <i>cis</i> -2-Cyclohexyl | — | — | 967 | 992 |
| <i>trans</i> -2-Cyclohexyl | 1044 | 985 | — | — |
| <i>cis</i> -4- <i>t</i> -Butyl | — | — | 955 | 1012 |
| <i>trans</i> -4- <i>t</i> -Butyl | 1060 | 980 | — | — |

* Overlapped.

It should be pointed out that the conformationally homogeneous *cis*- and *trans*-4-*t*-butylcyclohexanols show, in addition to the strong main band, a secondary weaker band at lower frequency. In *trans*-4-*tert*-butylcyclohexanol the main band occurs at 1062 cm^{-1} , and the secondary band occurs at 970 cm^{-1} . The *cis* isomer has the main band at 955 cm^{-1} , and the secondary band at 1012 cm^{-1} . In cyclohexanol the main band of the chair conformation (OH equatorial) occurring at 1065 cm^{-1} is accompanied by a weak band at 965 cm^{-1} which, however, overlaps with the main band of the axial conformation (955 cm^{-1}). This in turn is accompanied by a secondary band at 1025 cm^{-1} . In alkylcyclohexanols, the bands accompanying the equatorial conformation vary between 955 cm^{-1} and 980 cm^{-1} and those accompanying the axial conformation vary between 992 cm^{-1} and 1045 cm^{-1} [16]. In some instances, particularly in dialkylcyclohexanols, the main bands are doubled. In decalols equatorial isomers have the νOH frequency between $1025\text{--}1060\text{ cm}^{-1}$ with a secondary band in the range $971\text{--}1000\text{ cm}^{-1}$. The axial isomers have the main band at $937\text{--}964\text{ cm}^{-1}$ and the secondary band at $994\text{--}1022\text{ cm}^{-1}$ [16].

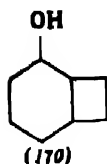
Frequencies in cyclopentanol and alkylcyclopentanol occur at the limit of equatorial and axial zones of cyclohexanols. Cyclopentanol has a strong band at 992 cm^{-1} and a weak band at 1028 cm^{-1} . The two bands occurring in the C—OH region in spectra of alkylcyclopentanol are shown in Table II-82.

For steric reasons or because of deformations due to the substituent, the hydroxyl group may adopt a *pseudo-equatorial* or *pseudo-axial* position. In

Table 11-82 $\nu\text{C}-\text{OH}$ frequencies in alkylcyclopentanol

| Compound | $\nu\text{C}-\text{OH}, \text{cm}^{-1}$ | |
|--|---|--------------|
| Cyclopentanol | 1028 w | 911 s |
| <i>cis</i> -2-Isopropylcyclopentanol | 1016 s | 995 w 968 |
| <i>trans</i> -2-Isopropylcyclopentanol | 1025 s | 985 w |
| <i>cis</i> -2-Cyclopentylcyclopentanol | 1019 w | 990 s |
| <i>trans</i> -2-Cyclopentylcyclopentanol | 1025 s | 974 w |

In this case the vibration frequency is less clearly defined than in cyclohexanols. Intermediate frequencies of ca. 990 cm^{-1} , observed for example, in cyclopentanol, place this absorption at the borderline between axial and equatorial regions [16].



OH groups in *endo* and *exo*-bicyclo [4. 2. 0] octanol-2 (170) have a *pseudo-axial* and *pseudo-equatorial* orientation, respectively [34]. The *endo* isomer has a weak absorption below 1000 cm^{-1} and the *exo* isomer has a strong absorption at 990 cm^{-1} (intermediate between equatorial OH (1069 cm^{-1}) and axial OH (955 cm^{-1}) absorption in cyclohexanol) [33]. In the *endo* isomer, the four-membered ring precludes the interconversion of *pseudo-axial* and *pseudo-equatorial* OH groups. In the *exo* isomer, where the four-membered ring does not have any influence on the hydroxyl group, the normal equilibrium between normal equatorial and axial conformations is reached.

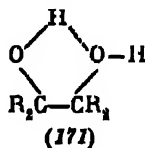
c. **O—H Deformation vibration.** The assignment of this vibration is uncertain [23]. The absorption occurs in the range $1300\text{--}1450 \text{ cm}^{-1}$. In methanol (in the vapor phase) the band occurs at 1340 cm^{-1} [35]; in ethanol, at 1393 cm^{-1} , and in propanol, at 1391 cm^{-1} [36]. The participation of the OH group in hydrogen bonding increases the frequency of the vibration. The 1340 cm^{-1} band in gaseous methanol disappears in solution and is replaced by a new band at 1420 cm^{-1} . The same phenomenon is observed also in other alcohols. In more complex structures, this band cannot be readily identified.

2. Di- and polyhydroxylic alcohols

Diols and polyols with OH groups sufficiently close to each other form intramolecular hydrogen bonds, along with previously described intermolecular hydrogen bonds. Compared with intermolecular hydrogen bonds, which in many instances make the investigation of the OH frequency difficult, intramolecular hydrogen bonds are important features in elucidations of structure.

There are two types of hydrogen bonds readily distinguishable in the infrared. As shown in monohydroxylic alcohols, the frequencies of intermolecular hydrogen bonds are concentration dependent. On dilution the band intensity decreases, and finally the band disappears. Intramolecular hydrogen bonds are independent of concentration. The bands arising from these absorptions persist even at high dilution. Generally, intermolecular hydrogen bonds give rise to broad bands (see above) whereas bands arising from intramolecular hydrogen bonds are sharp and well-defined. The frequency differences between free and associated νOH ($\Delta\nu$) are smaller in the case of intramolecular bonding than for intermolecular association.

Intramolecular hydrogen bonds can be observed in dilute solution di- and polyhydroxylic compounds (below 0.005M) in carbon tetrachloride, where no intermolecular bonds are formed. Under these conditions, it was observed that a number of cyclic and acyclic diols have two bands and others have a single band in the OH stretching mode region [37].



The band with the highest frequency ($3630\text{--}3644\text{ cm}^{-1}$ in acyclic diols and $3619\text{--}3636\text{ cm}^{-1}$ in cyclic diols) is assigned to the stretching vibration of the free O—H (see 177).

The second band is assigned to the hydroxyl group involved in intramolecular hydrogen bonding. This band is of variable frequency. The difference $\Delta\nu$ ($\nu\text{OH free} - \nu\text{OH assoc.}$) is a very precise measure of the distance between the two OH groups involved in intramolecular hydrogen bonding [37]. From this value one can estimate the force constant of the $\text{OH}\cdots\text{O}$ bond (the smaller the distance $\text{OH}\cdots\text{O}$, i.e., the stronger the hydrogen bond, the larger is the value of $\Delta\nu$) [38, 39].

a. **Acyclic diols.** The spectrum of ethylene glycol in dilute carbon tetrachloride solution shows two νOH bands, at 3644 cm^{-1} and 3612 cm^{-1} [37]. The first corresponds to the $\nu\text{O—H}$ stretching vibration of the free hydroxyl group and the second to the stretching vibration of the hydroxyl involved in the $\text{OH}\cdots\text{O}$ hydrogen bonding. In this case $\Delta\nu$ is 32 cm^{-1} . In general $\Delta\nu$ varies within large limits as a function of the relative positions of the two OH groups. In acyclic diols $\text{HO}-(\text{CH}_2)_n-\text{OH}$, where $n=2, 3, \dots, 7$, $\Delta\nu$ varies between 32 cm^{-1} (in ethylene glycol) and 156 cm^{-1} (in butanediol-1, 4) (Table II-83).

On theoretical grounds, of the two possible conformations for ethylene glycol (Fig. II-67), only the staggered *syn* conformation can form an intramolecular hydrogen bond.

The occurrence of a strong band arising from the intramolecular hydrogen bond shows that the molecule exists in the staggered *syn* conformation. The

energy of the hydrogen bond compensates for excess energy (5 kcal/mole) due to steric and dipolar repulsion of the two OH groups [40]. The small shift ($\Delta\nu = 2 \text{ cm}^{-1}$) shows that the hydrogen bond is weak. It increases in 1, 4-butanediol (156 cm^{-1}) where the steric proximity of the two OH groups favors hydrogen bonding.

Table II-83 νOH frequencies in acyclic diols

| $\text{HO}(\text{CH}_2)_n\text{OH}$ | free νOH | assoc. νOH | $\Delta\nu$ |
|---|---------------------|-----------------------|-------------|
| $\text{HO}(\text{CH}_2)_2\text{OH}$ | 3644 | 3612 | 32 |
| $\text{HO}(\text{CH}_2)_3\text{OH}$ | 3636 | 3558 | 78 |
| $\text{HO}(\text{CH}_2)_4\text{OH}$ | 3634 | 3478 | 156 |
| $\text{HO}(\text{CH}_2)_5\text{OH}$ | 3639 | — | — |
| $(\text{CH}_3)_2\text{COH}-\text{COH}(\text{CH}_3)_2$ | 3620 | 3583 | 43 |

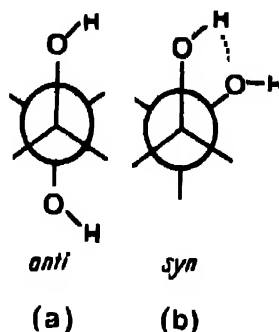


Fig. II-67 Staggered conformations of ethyleneglycol: (a) free OH; (b) associated OH.

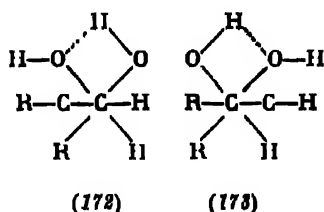
The effect of the volume of alkyl groups in determining the distance between OH groups was studied in various glycols, such as $\text{R}_2\text{COH}-\text{CH}_2\text{OH}$,

Table II-84 Free and bonded νOH frequencies, cm^{-1} [41]

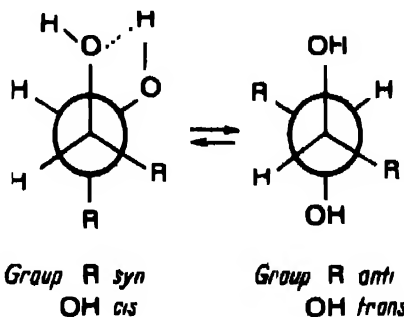
| R | νOH free | νOH bonded | $\Delta\nu$ |
|--|--------------------------------------|------------------------|-------------|
| | R_2COH | CH_2OH | |
| CH_3 | 3640 3620 | 3589 | 51 |
| C_2H_5 | 3640 3618 | 3586 | 54 |
| $(\text{CH}_3)_2\text{CH}$ | 3640 3630 <i>w</i> | 3570 | 70 |
| $(\text{CH}_3)_3\text{C}$ | 3636 | 3539 | 97 |
| | $\text{RCHOH}-\text{CHOHR}$ | | |
| CH_3 <i>meso</i> | 3633 | 3591 | 42 |
| <i>racemic</i> | 3632 | 3583 | 49 |
| $(\text{CH}_3)_2\text{CH}$ <i>meso</i> | 3635 | 3580 <i>w</i> | |
| <i>racemic</i> | 3633 | 3552 | 81 |
| $(\text{CH}_3)_3\text{C}$ <i>meso</i> | 3636 | | |
| <i>racemic</i> | 3637 | 3543 | 94 |
| | $\text{R}_2\text{COH}-\text{COHR}_2$ | | |
| CH_3 | 3620 | 3574 | 46 |
| C_2H_5 | 3622 | 3560 | 62 |
| $(\text{CH}_3)_2\text{CH}$ | 3631 | 3535 | 96 |
| $(\text{CH}_3)_3\text{C}$ | 3630 | 3460 | 170 |

meso and racemic, $R_2CHOH-CHOHR$, and $R_3COH-COHR_3$, where R = methyl, ethyl, isopropyl, and *tert*-butyl [41] (Table II-84).

In the glycol series $R_2COH-CH_2OH$, the 3640 cm^{-1} band corresponds to the primary OH and the 3620 cm^{-1} band corresponds to free tertiary OH. Associated OH bands occur at ca. 3585 cm^{-1} . The presence of three νOH bands shows that compounds with R = methyl, ethyl, and isopropyl exist in two conformations in equilibrium. In conformation (172), the primary hydroxyl forms a hydrogen bond with the tertiary OH group, whereas in conformation (173), the hydrogen of the tertiary OH group is involved in hydrogen bonding. In diols with isopropyl groups, the very low intensity of the tertiary νOH band shows that the conformation (173) is present in very small amounts. When the volume of the group R is large, the tertiary OH tends to adopt a conformation in which the hydrogen atom is remote from the alkyl groups. This is achieved by its bonding to the primary OH group. Such an orientation favors structure (173).



meso



In the racemic series of 1,2-disubstituted glycols $RCHOH-CHOHR$, all compounds exist in a conformation in which the OH groups are *cis* to each other (R group *anti*) (Fig. II-68). The spectrum has two bands, free νOH and bonded νOH (Table II-84).

racemic

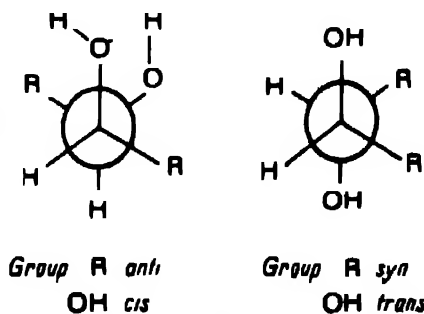
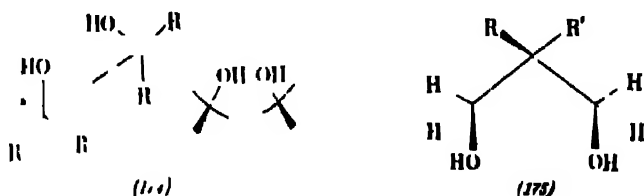


Fig. II-68 Staggered conformations of 1,2-di-alkylethyleneglycols.

In the meso series, when R = methyl or ethyl, the OH groups are *cis* to each other; when R = isopropyl, the predominant conformation is that with the OH groups *trans* (the band arising from intramolecular bonding is weak). Compounds with R = *tert*-butyl exist exclusively in the *trans* conformation (R *anti*). Table II-84 shows that in compounds $R_2COH-COHR_2$, the difference $\Delta\nu$ increases with the volume of R . When R = *tert*-butyl (174), $\Delta\nu OH$ has the highest value (170 cm^{-1}). It was suggested that the repulsion between the four methyl groups results in a deformation of the molecule





which brings the two OH groups closer to each other [41]. $\Delta\nu$ values in substituted 1,3-propanediols vary between 52 and 113 cm^{-1} . The value in 1,3-propanediol ($\Delta\nu_{\text{OH}} = 78 \text{ cm}^{-1}$) is small cf. 1,4-butanediol (156 cm^{-1}).

For a number of 1,3-propanediols $\text{RR}'\text{C}(\text{CH}_2\text{OH})_2$, mean $\Delta\nu_{\text{OH}}$ values are given in Table II-85 [42].



In monosubstituted compounds (175) $\text{R}=\text{H}$, $\text{R}'\neq\text{H}$, the volume of substituent R' does not preclude the formation of a hydrogen bond ($\Delta\nu$ has ap-

Table II-85 ν_{OH} values in $\text{RR}'\text{C}(\text{CH}_2\text{OH})_2$ [42]

| R | R | $\Delta\nu_{\text{OH}}$ (mean value)* cm^{-1} |
|---|------------------------|---|
| H | H | 78 |
| H | Primary alkyl | 85 |
| H | Secondary alkyl | 84 |
| H | Tertiary alkyl | 85 |
| CH_3 | Primary alkyl | 88 |
| CH_3 | Secondary alkyl | 86 |
| CH_3 | Tertiary alkyl | 89 |
| C_6H_5 | Primary alkyl | 89 |
|  | CH_2OH | 68 |
|  | CH_2OH | 85 |
|  | CH_2OH | 86 |
|  | CH_2OH | 89 |

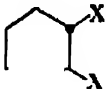
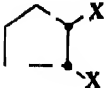
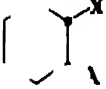
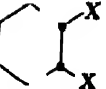
* Free ν_{OH} with frequencies 3637–3640 cm^{-1} was taken as standard.

proximately the same value). In 2, 2-disubstituted compounds, $\Delta\nu_{\text{OH}}$ increases slightly. However, if one of the substituents is a tertiary group, $\Delta\nu$ decreases. It is thought that in this case the bulky group draws the two OH groups further apart.

If R and R' in formula (175) are three- or four-membered cycloalkane rings (see Table II-85) $\Delta\nu$ decreases [43].

The effect of substituents in 1, 4-diols is completely different from that in 1, 2-diols [44]. The interaction between the two OH groups in the 1, 4-positions is favored. In 1, 4-butanediol the difference between the free ν_{OH} frequency (3636 cm^{-1}) and the bonded ν_{OH} frequency (3477 cm^{-1}) is 159 cm^{-1} (Fig. II-69).

Table II-86 $\Delta\nu_{\text{OH}}$ values in 1,2- and 1,4-cycloalkane diols

| Compound | X=OH (1,2-diols) | X=CH ₂ OH (1,4-diols) |
|--|---------------------|-------------------------------------|
|  <i>trans</i> | 0 | 159 |
|  <i>cis</i> | 61 | 131 |
|  <i>trans</i> | 33 | 136 |
|  <i>cis</i> | 38 | 114 |

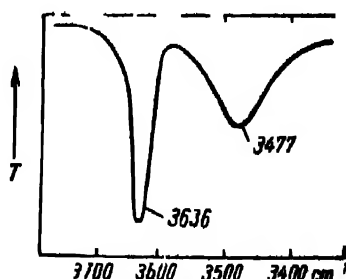










Fig. II-69 Infrared spectrum of 1,4-butanediol; 0.005 M solution in CCl_4 [44]

It should be pointed out that in contrast to 1,2-diols (see Table II-81) in *meso*-isomers $\Delta\nu$ is larger than in racemic isomers. Cyclic compounds show a similar behavior. In cycloalkane-1, 2-dimethanols (1, 1-diols), $\Delta\nu$ is larger in *trans* than in *cis* isomers which is opposite to 1,2-dihydroxycycloalkanes [16] (see Table II-86).

A larger volume of the substituent in 2, 3-disubstituted 1, 4-diols results in increased $\Delta\nu$ values, similar to the 1,2-diol series [41]. In 2, 2, 3, 3-tetra-*n*-butyl-butandiol-1, 1, $\Delta\nu = 196\text{ cm}^{-1}$, comparable to 1, 1, 2, 2-tetra-*t*-butyl-ethanediol-1, 2 ($\Delta\nu = 170\text{ cm}^{-1}$). The strength of the hydrogen bond expressed in terms of $\Delta\nu_{\text{OH}}$ values is an efficient tool for establishing the conformation (Tables II-86 and II-87).

In the cycloalkene series the situation is slightly different. 1, 2-Dimethanolcyclobutene-3 (planar ring) and 1,2-dimethanolbicycloheptene (a rigid system) do not differ from saturated analogs. However, in the six-membered

Table II-87 $\Delta\nu$ Values in mono- and bicyclic-1,4-diols [44]

| | | | ν_{OH} free | ν_{OH} bonded | $\Delta\nu_{OH}$ |
|---|--------------------|-----------------|--------------------|----------------------|------------------|
|  | <chem>CH2OH</chem> | <i>cis</i> | 3634 | 3507 | 127 |
| | <chem>CH2OH</chem> | <i>trans</i> | 3635 | 3498 | 137 |
|  | <chem>CH2OH</chem> | <i>cis</i> | 3632 | 3501 | 131 |
| | <chem>CH2OH</chem> | <i>trans</i> | 3634 | 3475 | 159 |
|  | <chem>CH2OH</chem> | <i>cis</i> | 3634 | 3502 | 132 |
| | <chem>CH2OH</chem> | <i>trans</i> | 3635 | 3533* | 101 |
| | <chem>CH2OH</chem> | | | 3491 | 144 |
| | <chem>CH2OH</chem> | | | 3531* | 101 |
|  | <chem>CH2OH</chem> | <i>endo-cis</i> | 3623 | 3498 | 125 |
| | <chem>CH2OH</chem> | <i>exo-cis</i> | 3623 | 3487 | 136 |
| | <chem>CH2OH</chem> | <i>trans</i> | 3635 | 3496 | 139 |
|  | <chem>CH2OH</chem> | <i>cis</i> | 3623 | 3490 | 133 |
| | <chem>CH2OH</chem> | <i>trans</i> | 3630 | 3477 | 159 |
|  | <chem>CH2OH</chem> | <i>cis</i> | 3623 | 3498 | 125 |
| | <chem>CH2OH</chem> | <i>trans</i> | — | — | — |
|  | <chem>CH2OH</chem> | <i>cis</i> | 3638 | 3551 | 87 |
| | <chem>CH2OH</chem> | | | 3472 | 166 |
| | <chem>CH2OH</chem> | <i>trans</i> | 3636 | 3534 | 102 |
| | <chem>CH2OH</chem> | | | 3517 | 119 |
|  | <chem>CH2OH</chem> | <i>endo-cis</i> | 3625 | 3494 | 131 |
| | <chem>CH2OH</chem> | <i>exo-cis</i> | 3623 | 3487 | 136 |
| | <chem>CH2OH</chem> | <i>trans</i> | 3636 | 3503 | 133 |

* Shoulder

ring, the variation is reversed. In the saturated series, $\Delta\nu$ is smaller in the *cis* isomer than in the *trans*.

In the unsaturated series (e.g. 4-cyclohexene-1, 2-dimethanol), $\Delta\nu$ is larger than $\Delta\nu$ trans.

b. **Cyclic diols, cycloalkanediols.** The ν OH vibration is of special value in establishing the conformation of stereoisomeric cyclic diols. ν OH frequencies of some five- and six-membered cyclic 1, 2-diols are shown in Table II-88.

Table II-88 ν OH frequencies (cm^{-1}) in cyclic diols*

| Cyclic diol | free ν OH | bonded ν OH (intramolecular) |
|--|---------------|-------------------------------------|
| <i>cis</i> -1, 2-cyclopentanediol | 3633 | 3572 |
| <i>trans</i> -1, 2-cyclopentanediol | 3620 | — |
| <i>cis</i> -1, 2-cyclohexanediol | 3626 | 3587 - 3405** |
| <i>trans</i> -1, 2-cyclohexanediol | 3634 | 3602 |
| <i>cis</i> -1, 3-cyclohexanediol | 3619 | 3544 |
| <i>trans</i> -1, 3-cyclohexanediol | 3620 | — |
| <i>cis</i> -1, 4-cyclohexanediol | 3629 | — |
| <i>trans</i> -1, 4-cyclohexanediol | 3630 | — |
| <i>cis</i> -1, 2-tetrahydronaphthalenediol | 3618 | 3575 |
| <i>trans</i> -1, 2-tetrahydronaphthalenediol | 3608 | — |
| <i>trans</i> -9, 10-dihydroanthracenediol | 3607 | — |
| <i>cis</i> -9, 10-dihydrophenanthrenediol | 3605 | 3567 |

* 0.005M CCl_4 solution; LiBr prism.

** solid.

In *cis*-1, 2-cyclohexanediol (chair form), one of the two OH groups is axial (*a*) and the other equatorial (*e*) (176). In the *trans* isomer both groups can be either axial (*a*, *a*) (177) or equatorial (*e*, *e*) (178) [45].

If one uses normal values for interatomic distances and angles ($\text{C}-\text{C}$: 1.54 Å, $\text{C}-\text{O}$: 1.42 Å, $\text{O}-\text{H}$: 0.96 Å and $\angle\text{CCO}$: $109^\circ 28'$, $\angle\text{COH}$: 108°), the calculated $-\text{O}-\text{H} \cdots \text{O}-$ distance in *cis*-1, 2-cyclohexanediol is 2.31 Å. The spectrum (Fig. II-70) shows two bands: free ν OH at 3626 cm^{-1} and bonded ν OH at 3588 cm^{-1} ($\Delta\nu = 39 \text{ cm}^{-1}$).

In *trans*-1, 2-cyclohexanediol, the distance $-\text{OH} \cdots \text{O}$ calculated for the axial conformation is greater than 3.3 Å, and for the equatorial conformation (*e*, *e*) it is 2.31 Å (see Table II-89). The spectrum shows

the bonded OH band at 3602 cm^{-1} , at a distance of 32 cm^{-1} from the free OH band (3634 cm^{-1}). Consequently, the molecule exists in the equatorial conformation, which is also energetically more favored.

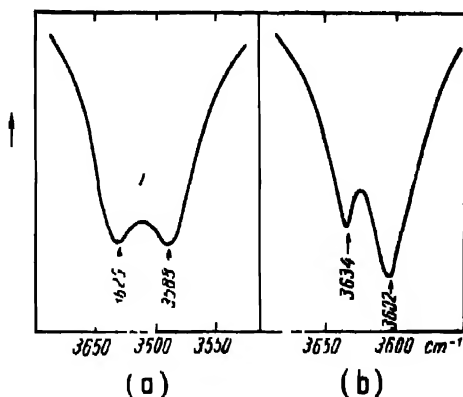
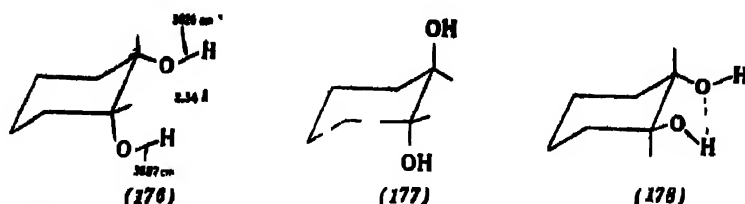


Fig. II-70 (a) Infrared spectrum of *cis*-1,2-cyclohexanediol (176) and (b) *trans*-1,2-cyclohexanediol (178).

In 1, 3-cyclohexanediols, only the *cis* isomer (179) can form intramolecular hydrogen bonds. In the axial form (*a, a*), the calculated distance is 1.64 Å.



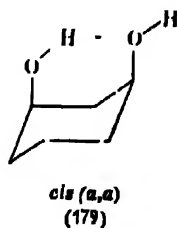
In the *e, e-cis* form, the distance is greater than 3.3 Å. In this case the $\Delta\nu$ - value is large (75 cm^{-1}), corresponding to stronger hydrogen bonds, i.e., to a shorter $\text{-OH} \cdots \text{O}$ distance. This means that the intramolecular hydrogen bond supplies enough energy to keep the hydroxyl group in the axial position.

Table II-89 $\Delta\nu_{\text{OH}}$ values in cyclic diols

| Diol | Conformation | $\Delta\nu_{\text{OH}}$ cm^{-1} | $\text{OH} \cdots \text{O}$ Å |
|-------------------------------------|--------------|---|----------------------------------|
| <i>cis</i> -1, 2-cyclopentanediol | — | 61 | 1.81 |
| <i>trans</i> -1, 2-cyclopentanediol | — | 0 | 1.3 |
| <i>cis</i> -1, 2-cyclohexanediol | <i>a, e</i> | 38 | 2.34 |
| <i>trans</i> -1, 2-cyclohexanediol | <i>e, e</i> | 32 | 2.31 |
| | <i>a, a</i> | — | 3.34 |
| <i>cis</i> -1, 3-cyclohexanediol | <i>a, a</i> | 75 | 1.64 |
| | <i>e, e</i> | — | 3.3 |
| <i>trans</i> -1, 3-cyclohexanediol | <i>a, e</i> | — | 3.3 |
| <i>cis</i> -1, 4-cyclohexanediol | <i>a, e</i> | — | 3.3 |
| <i>trans</i> -1, 4-cyclohexanediol | <i>a, a</i> | — | 3.3 |
| | <i>e, e</i> | — | — |

Table II-89 shows the calculated $\text{OH} \cdots \text{O}$ distances for stereoisomeric 1, 2-cyclopentanediois and cyclohexanediols. From the observed $\Delta\nu$ values, it follows that only when the distance between the OH groups is shorter than 3.3 Å can they form hydrogen bonds. As $\Delta\nu$ increases, the $\text{OH} \cdots \text{O}$ distance decreases. The following empirical relation was established by relating the distance $\text{OH} \cdots \text{O}$ to the $\Delta\nu$ value:

$$l_{\text{OH} \cdots \text{O}} = \frac{250 \cdot 10^{-8}}{\Delta\nu} - 75.$$



This relation enables the calculation of the OH...O distance ($\log \dots$) in angstroms [37, 46]; for example, in *cis*-1,2-cyclohexanediol, $\Delta\nu$ (38 cm^{-1}) is larger than in the *trans* isomer ($\Delta\nu=32 \text{ cm}^{-1}$). The calculated OH...O distance is the same for both isomers (2.34 Å, see Table II-89). By applying the above relationship, a distance of 2.38 Å results for the *trans* isomer (e, e) which explains why hydrogen bonds are formed less readily, cf. the *cis* isomer (a, e).

In *cis*-1,2-cyclopentanediol (180), $\Delta\nu=61 \text{ cm}^{-1}$ corresponds to a OH...O distance of 1.84 Å.

In cyclic 1,2-diols with rings from 5 to 16 carbon atoms, $\Delta\nu$ values vary with ring size [46] (Table II-90).

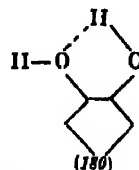
Table II-90 νOH frequencies (cm^{-1}) in cyclic diols [46]

| 1,2-Diol | νOH free | νOH bonded | $\Delta\nu$ |
|-------------------------------|------------------------|--------------------------|-------------|
| <i>cis</i> -cyclopentane | 3633 | 3572 | 61 |
| <i>trans</i> -cyclopentane | 3620 | - | - |
| <i>cis</i> -cyclohexane | 3628 | 3588 | 38 |
| <i>trans</i> -cyclohexane | 3639 | 3600 | 33 |
| <i>cis</i> -cycloheptane | 3632 | 3588 | 44 |
| <i>trans</i> -cycloheptane | 3626 | 3589 | 37 |
| <i>cis</i> -cyclooctane | 3635 | 3584 | 51 |
| <i>trans</i> -cyclooctane | 3631 | 3588 | 43 |
| <i>cis</i> -cyclononane | 3631 | 3582 | 49 |
| <i>trans</i> -cyclononane | 3632 | 3587 | 45 |
| <i>cis</i> -cyclodecane | 3629 | 3585 | 44 |
| <i>trans</i> -cyclodecane | 3633 | 3588 | 45 |
| <i>cis</i> -cyclododecane | 3629 | 3591 | 38 |
| <i>trans</i> -cyclododecane | 3635 | 3584 | 51 |
| <i>cis</i> -cyclohexadecane | 3632, 3626 | 3591, 3587 | - |
| <i>trans</i> -cyclohexadecane | 3635 | 3585 | 50 |

In *trans*-diols $\Delta\nu$ increases with ring size, reaching a maximum value of 50 cm^{-1} in the twelve-membered ring. In *cis*-diols, a plot of the variation in $\Delta\nu$ with ring size shows a minimum for the six-membered ring and a maximum for the eight- and twelve-membered rings.

The conclusion drawn is that in 1,2-diols with rings larger than 10 atoms, OH groups in *trans* isomers are closer in space than in *cis* isomers. In rings smaller than cyclodecane, the OH groups are closer in *cis* isomers [46].

The strongest hydrogen bonds are formed in *cis*-1,2-cyclopentanediol, where the two OH groups are almost eclipsed. In *trans*-1,2-cyclopentanediol, the OH groups are too far apart to form hydrogen bonds (Table II-90). In



six- to nine-membered rings, the *cis* diol forms stronger bonds than the *trans* isomer. This shows that the *cis* OH group is easier to distort. In the ten-membered ring the differences are minute and in the twelve-membered ring, the OH groups are closer in the *trans* isomer than in the *cis* isomer. This behavior can be explained if one allows that in large rings the *trans* diol adopts the *anti* staggered conformation of butane (Fig. II-71a). In this case the two hydroxyls are close in space. The change to the staggered *syn* forms is easy, because in these rotations the ring carbon is not eclipsed.

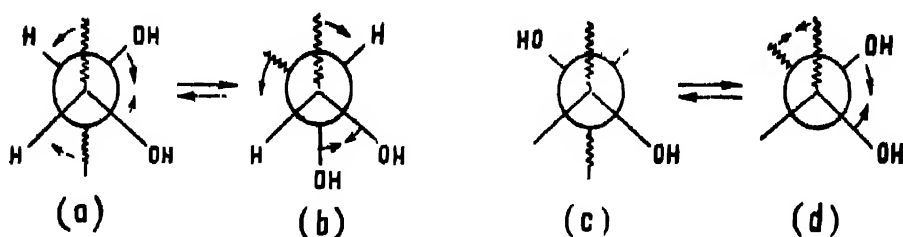


Fig. II-71 Conformation of large ring 1,2-cycloalkanediois.

In the *cis* isomer, the *anti* staggered conformation (Fig. II-71c) does not form hydrogen bonds. In the *syn* staggered conformation (Fig. II-71d), the hydroxyl groups come closer by eclipsing the ring carbon [46].

Table II-91 ν_{OH} values in some cyclohexanediols [47]

| Compound | Conformation | Free ν_{OH} cm^{-1} | Bonded ν_{OH} cm^{-1} |
|---------------------------------|-------------------------------------|-------------------------------------|---------------------------------------|
| <i>cis</i> | | | |
| cyclohexanediol-1, 2 | <i>a, e</i> | 3626 | 3588 |
| 1-methylcyclohexanediol-1, 2 | <i>a, e</i> | 3628 | 3584 |
| 1-ethylcyclohexanediol 1, 2 | <i>a, e</i> | 3628 | 3583 |
| 1-isopropylcyclohexanediol 1, 2 | <i>a, e</i> | 3629 | 3582 |
| <i>trans</i> | | | |
| cyclohexanediol 1, 2 | <i>e, e</i> | 3631 | 3600 |
| 1-methylcyclohexanediol 1, 2 | <i>e, e</i> | 3618 | 3597 |
| 1-ethylcyclohexanediol-1, 2 | <i>a, a \rightleftharpoons e, e</i> | 3627 | 3600 |
| | | 3618 | |
| 1-isopropylcyclohexanediol-1, 2 | <i>a, a</i> | 3625 | — |

The frequencies of free and bonded OH stretching vibrations have been used to determine stable conformations in a number of cyclohexanediols where substituents compete for the equatorial position [47].

Studies of infrared spectra of *cis*- and *trans*-1-methyl (181), 1-ethyl (182), and 1-isopropylcyclohexanediol-1,2 (183) enabled us to establish the equatorial, the axial conformation of the secondary OH versus the tertiary OH, hence the axial or equatorial orientation of the alkyl group. From ν_{OH} frequencies it could be also inferred which O—H group is involved in intramolecular hydrogen bonding. The observed ν_{OH} frequencies are shown in Table II-91 (The free ν_{OH} frequency was compared with OH frequencies in axial secondary monoalkylcyclohexanol (3627–3632 cm^{-1}), equatorial secondary (3622–3623 cm^{-1}), axial tertiary (3618 cm^{-1}), and equatorial tertiary (3613 cm^{-1}).

The energy of the hydrogen bond between the two equatorial OH groups in 1-methyl-*trans*-cyclohexanediol-1, 2 (181) is sufficient to maintain the CH_3 group in axial position. In the spectrum (Fig. II-72), the free OH frequency corresponds to the tertiary OH group at 3618 cm^{-1} . The frequency of the associated OH band is 3597 cm^{-1} . Consequently, the two OH groups are equatorial and the hydrogen atom of the secondary OH is involved in bonding.

In 1-ethyl-*trans*-cyclohexanediol-1, 2 (182), the ethyl group competes for the equatorial position. The spectrum shows a mixture of the two isomers,

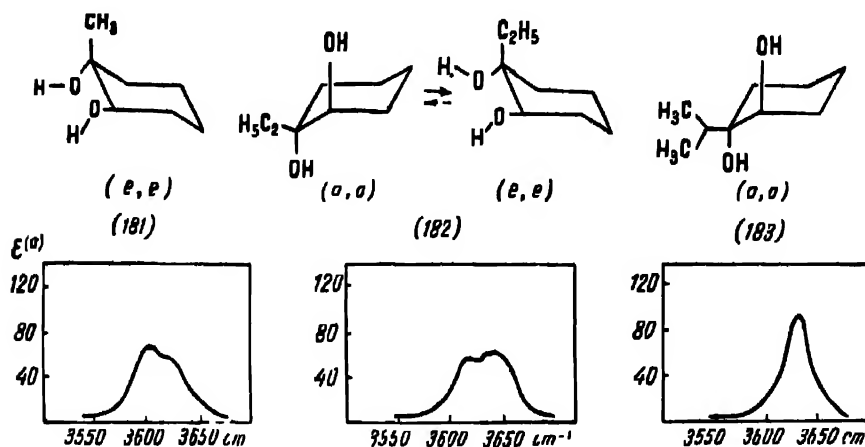


Fig. II 72 Infrared spectra of alkylcyclohexanediols (181), (182), and (183) in the OH stretching vibration region (in CCl_4)

namely, a compound with two axial hydroxyl groups and an equatorial ethyl group and another one with the two equatorial OH groups and an axial ethyl group.

The α, α isomer does not form an intramolecular hydrogen bond, and the spectrum shows the frequencies of the free secondary and tertiary hydroxyl,

at 3627 cm^{-1} and 3618 cm^{-1} , respectively. It is believed that the bond is formed by the hydrogen atom of the secondary hydroxyl. The bulkier isopropyl group in 1-isopropyl-*trans*-cyclohexanediol-1, 2 (188) occupies the equatorial position exclusively forcing the two hydroxyl groups into axial positions. They cannot form hydrogen bonds, and the spectrum shows a single unresolved band at 3625 cm^{-1} , containing both the secondary axial νOH and the tertiary νOH (Fig. II-72).

This study [47] shows that in *trans*-1, 2-diols the secondary equatorial hydroxyl is preferentially involved in intramolecular hydrogen bonding. The frequency of the free hydroxyl corresponds to a tertiary OH group (3618 cm^{-1}) (182). In the stereoisomeric *cis*-1, 2-diols with one axial and one equatorial OH group, the equatorial hydroxyl is involved in hydrogen bonding, whether it is secondary or tertiary. The frequency of the free νOH is 3628 cm^{-1} (axial) (Table II-91).

Spectra of secondary *trans*-1,2-diols of 1-methyl-4-isopropylcyclohexane (184–186) show that the methyl and isopropyl groups are preferentially equatorial and the OH groups axial [20, 17] (Fig. II-73).

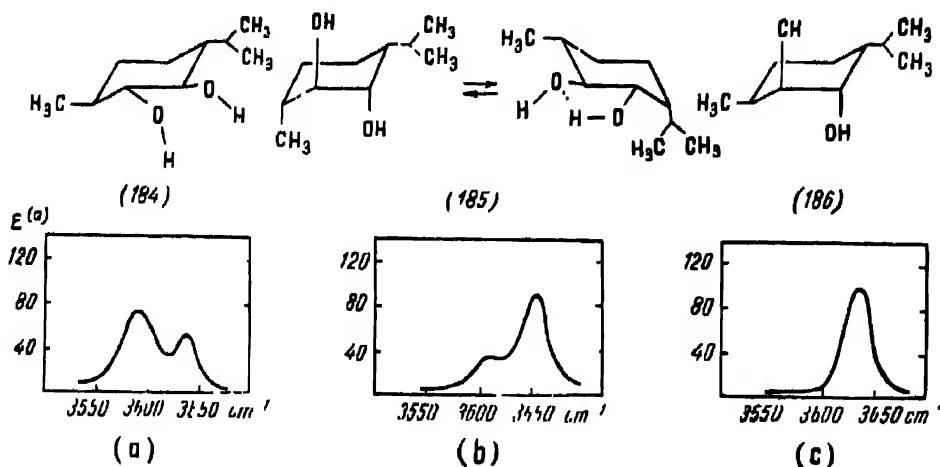


Fig. II-73 Infrared spectra of 1-methyl-4-isopropyl-1,2-*trans*-diols in the O - H stretching vibration region (in CCl_4) [17].

(a) (184), (b) (185), and (c) (186).

In 1, 2-dihydroxytetraline and 9, 10-dihydroxy-9, 10-dihydrophenanthrene, only *cis* isomers form hydrogen bonds [37].

$\Delta\nu\text{OH}$ values were used to establish the conformations of some diols in the tetraline [48], decaline [49, 50], and perhydroindane [51] series, shown in Table II.92.

c. **Intermolecular hydrogen bonds.** At higher concentrations, infrared spectra of diols show a third band arising from the intermolecular hydrogen bonding of the hydroxyl group. This new absorption shows all the characteristics observed in monohydroxylic alcohols (strong, broad bands). The extinction coefficient falls on dilution and is practically zero at concentrations below 0.004M. The intermolecular association of diols results in a larger shift of the νOH band than intramolecular bonding or dimerization by means of hydrogen bonds. The free νOH frequency in diols is ca. 3626 cm^{-1} . The intramolecularly bonded OH group absorbs at ca. 3583 cm^{-1} , and the intermolecularly bonded OH, at 3477 cm^{-1} .

The OH groups in diols can form hydrogen bonds in the presence of molecules acting both as proton donors and acceptors.

Table II-22 νOH values and the conformation of some diols

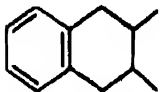
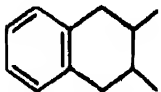
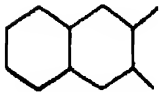
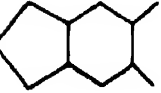
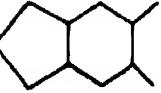
| Diols | OH position | free νOH | bonded νOH | $\Delta\nu$ | Conformation |
|---|-------------------------|---------------------|-----------------------|-------------|--------------|
|  | OH | | | | |
| | 2,3 | 3622 | 3590 | 32 | <i>cis</i> |
|  | OH | | | | |
| | 2,3 | 3630 | 3598 | 32 | <i>trans</i> |
|  | OH | | | | |
| | 2 β , 3 β | 3625 | 3592 | 33 | <i>cis</i> |
| | 2 α , 3 α | 3632 | 3587 | 45 | <i>cis</i> |
| | 2 α , 3 β | 3627 | 3597 | 30 | <i>trans</i> |
|  | OH | | | | |
| | 5,6 | 3623 | 3597 | 14 | <i>cis</i> |
|  | OH | | | | |
| | 5,6 | 3627 | 3594 | 33 | <i>trans</i> |

Figure II-74 shows the absorption spectra of pinacol ((187), $\text{R} = \text{CH}_3$) in 0.006M solution containing only the free and intramolecularly bonded νOH bands (Curve 1) and in 0.05M solution where all three types of bands are present (Curve 3). Curve 2 represents the spectrum of a 0.0006M solution with added HCl and Curve 4 a 0.05M solution in ethyl ether.

On adding ether (hydrogen acceptor) the intensity of the free hydroxyl band falls substantially, intramolecular νOH is practically unchanged and

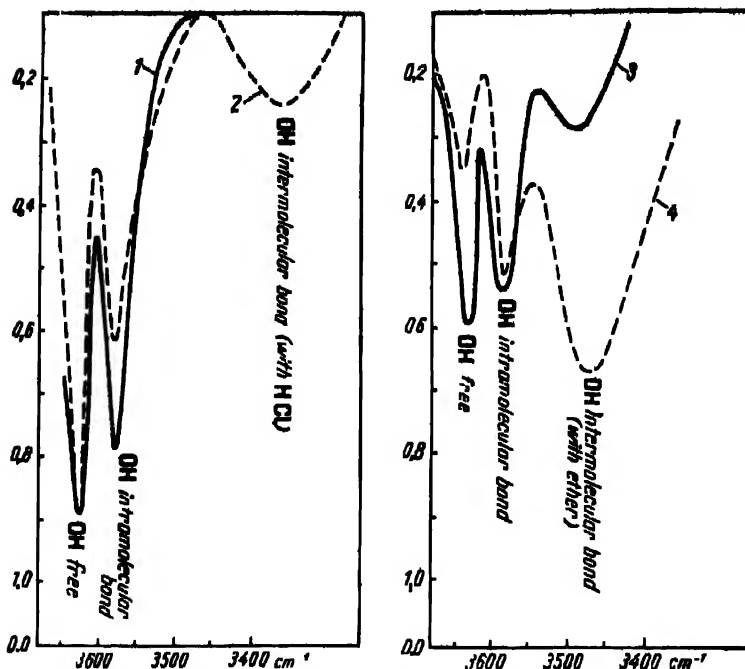
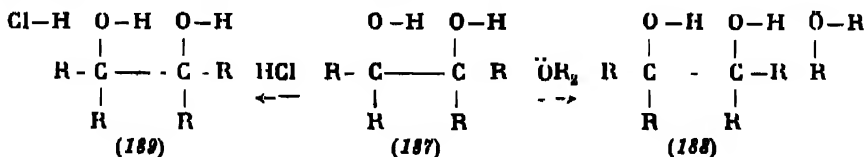


Fig. 11-74 Infrared spectrum of pinacol in the OH stretching vibration region.

(1) 0.006 M solution in CCl_4 ; (2) in the presence of HCl; (3) in 0.05 M solution; (4) in the presence of ethyl ether.

the band arising from intermolecular hydrogen bonds becomes stronger due to association between alcohol and ether molecules (188).



On adding HCl (hydrogen donor) the new hydrogen bond is formed with the oxygen atom not involved in intramolecular association (189). The free νOH band remains unchanged, whereas the intensity of the intramolecularly bonded νOH decreases, because of its additional involvement in the intermolecular bonding between alcohol and hydrochloric acid [37].

3. Mono- and polyhydroxylic phenols

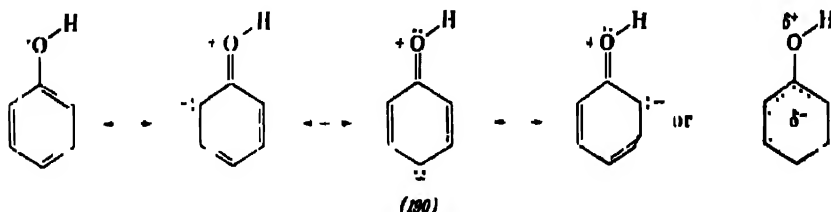
The frequency of the free OH stretching vibration in phenols lies in the range $3594\text{--}3615\text{ cm}^{-1}$ [37, 52, 53]. In dilute solutions of phenol and alkylphenols in nonpolar solvents (CCl_4 , C_6Cl_6), the band arises at $3612 \pm$

$\pm 2 \text{ cm}^{-1}$ [53]. Alkyl groups in the *meta* or *para* position do not alter the frequency of this vibration [54, 55]. However, *ortho*-disubstituted alkyl phenols absorb at higher frequencies [56]. In the vapor phase the frequencies are higher. Phenol absorbs at 3655 cm^{-1} and alkylphenols, between 3655 and 3670 cm^{-1} [57].

The decrease in νOH frequency in phenols (cf. alcohols) is due to conjugation between the unshared electrons of the OH oxygen and the π electrons of the aromatic ring (190) [58]. This results in a decrease in the O—H bond force constant and a simultaneous increase of the C—O bond order.

Phenols form intermolecular hydrogen bonds more readily than alcohols. The interaction between the phenolic OH and various electron donors has been studied extensively. The hydroxyl group in associated phenol absorbs at $3300\text{--}3500 \text{ cm}^{-1}$ (dimers at ca. 3500 cm^{-1} and polymers at ca. 3320 cm^{-1} [52, 59]).

As in alcohols, the value of the $\Delta\nu$ shift of the νOH band provides information on the strength of the hydrogen bond and the type of association [59].



It was shown that in concentrated solution *meta* and *para* substituted monoalkylphenols, form polymeric associations absorbing at 3322 cm^{-1} ($\Delta\nu=47 \text{ cm}^{-1}$). The strength of the hydrogen bond (evaluated from $\Delta\nu$) is not influenced by the nature or volume of the substituent ($\Delta\nu$ is the same for alkyl groups such as methyl or *tert*-butyl or for OH, NH_2 , Cl, etc.) [59].

In 2- or 2, 6-substituted phenols the νOH frequencies are shifted by virtue of steric hindrance of the substituent. By comparing the $\Delta\nu\text{OH}$ value in phenols with that in alcohols, alkylphenols have been classified as sterically hindered, partially hindered, and normal [60–63]. *ortho*-Disubstituted phenols with bulky alkyl groups (e.g., di-*tert*-butylphenol) do not have absorptions in the bonded νOH region, which is in agreement with the chemical properties of the OH group in these compounds. The spectrum shows a single strong band of the free hydroxyl, at 3643 cm^{-1} [56, 57, 59]. Substituted phenols with a single alkyl group in the *ortho* position have a much smaller $\Delta\nu$ value than sterically normal phenols [59, 62, 63]. It was assumed that these molecules are associated as dimers [59].

Spectra of 2-*tert*-alkylphenols show two absorptions in the free νOH region [56, 57, 64]; for example, 2-*tert*-butylphenol has a strong band at 3605 cm^{-1} and a weak band at 3643 cm^{-1} (Fig. II-75). The frequency of the first band corresponds to the OH band in free phenol. The second, weaker band has the same frequency as that of the OH group in 2, 6-di-*tert*-butylphenol (3643 cm^{-1}). This was explained by the coexistence of the two geometrical isomers *cis* (191) and *trans* (192). Consequently, the O—H bond in the hydroxyl group which is coplanar with the benzene ring can be oriented toward the *tert*-butyl group or in the opposite direction [56, 57].

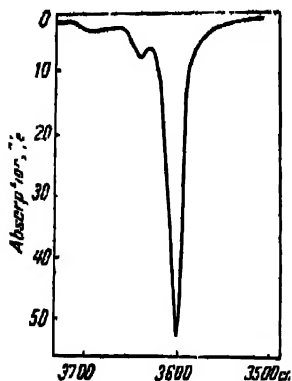
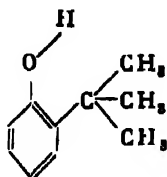
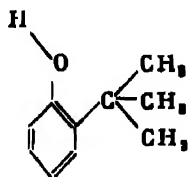


Fig. II-75 Infrared spectrum of 2-*tert*-butylphenol (solution in CCl_4) in the νOH stretching vibration region.



(191)

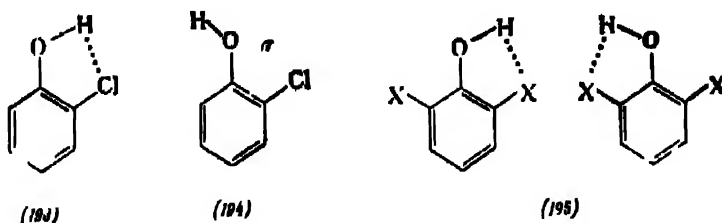


(192)

The lower frequency band, analogous to that of free phenols corresponds to the *trans* configuration (192) and the weak higher frequency band, analogous to 2, 6-di-*tert*-butylphenol corresponds to the *cis*-configuration (191). By measuring the intensities of the two absorptions it was determined that 2-*tert*-butylphenol contains ca. 6% *cis*-form [56]. *Cis-trans* isomerism is maintained both in the vapor phase and in solution [57]. Frequency and band intensity have been extensively studied in a number of *o-tert*-alkylphenols [56, 57]. It should be pointed out that the OH frequency in 2, 6-di-*tert*-butylphenol (3643 cm^{-1}) is higher ($+33\text{ cm}^{-1}$) than that of normal phenols. This cannot be explained solely by the $-\text{I}$ effect of the alkyl groups (which exist in the *meta* and *pura* positions as well and where the frequency is normal). A more complicated steric interaction between the hydrogen atom of the O—H group and the alkyl group has to be taken into account.

Spectra of substituted phenols with electron-donating atoms or groups in the *ortho* position, capable of forming hydrogen bonds with the phenolic OH show, along with free νOH bands, bands arising from intramolecularly bonded OH. In this case the bonded OH band has a lower frequency. The intramolecular hydrogen bond in *o*-halophenols was considered as proof for the $p\text{-}\pi$ conjugation in phenols, possible only if the OH group is coplanar with the benzene ring [65]. Spectra of dilute solutions of *o*-chlorophenol show two bands (at 3609 and 3547 cm^{-1}). They were explained [65] by the existence of an intramolecular hydrogen bond of the *cis*-form (193), more stable than the *trans* form (194) by 2–3 kcal/mole.

The higher frequency band (3609 cm^{-1}) is assigned to the free OH vibration of the *trans* form and the lower frequency band (3547 cm^{-1}) arises from



the intramolecularly bonded hydroxyl ($\text{O}-\text{H} \dots \text{Cl}$), possible only in the *cis* isomer. The same phenomenon occurs in *o*-bromo- and *o*-iodophenols [66] (Table II-93).

In 2, 6-dibromophenols the two structures are equivalent (195). The spectrum shows a single band arising from the intramolecularly bonded hydroxyl.

Di- and polyhydroxylic phenols with adjacent OH groups form intramolecular hydrogen bonds. Catechol (196) (in dilute solution) shows two bands, at 3612 cm^{-1} (free νOH) and 3568 cm^{-1} (intramolecularly bonded νOH) [53].

In *o*-diphenols substituted with alkyl, Cl or NH_2 groups the bands occur at 3610 ± 5 and $3560 \pm 10\text{ cm}^{-1}$ (Table II-94).

Table II-93 OH frequencies in halophenols

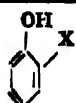
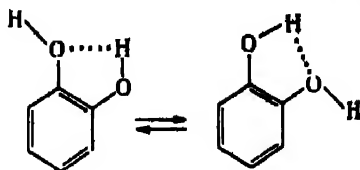
|  | free νOH cm^{-1} | bonded νOH cm^{-1} |
|---|---|---|
| F | — | 3592 |
| Cl | 3609 | 3547 |
| Br | 3604 | 2529 |
| I | 3600 | 3527 |

Table II-94 νOH frequencies (cm^{-1}) in substituted phenols and catechols [53]

| Substituent | Phenol free νOH | Catechol | |
|---------------------------------------|-------------------------------|---------------------|-----------------------|
| | | free νOH | bonded νOH |
| 4- OCH_3 | 3615 | 3608 | 3561 |
| 4-OH | 3615 | — | — |
| 4- $\text{C}(\text{CH}_3)_3$ | 3612 | 3612 | 3569 |
| 4- CH_3 | 3612 | 3612 | 3569 |
| 1-H | 3610 | 3612 | 3568 |
| 4- C_6H_5 | 3609 | 3608 | 3567 |
| 1- $\text{C}(\text{C}_6\text{H}_5)_3$ | — | 3608 | 3568 |
| 4-Cl | 3608 | 3606 | 3564 |
| 4- COOC_2H_5 | 3601 | — | — |
| 4- NO_2 | 3594 | 3592 | 3550 |



(196)

OH frequencies of substituted phenols and catechols in dilute CCl_4 solution are compared in Table II-94.

4. Functional derivatives of alcohols

a. Ethers

Ethers have characteristic C—O—C bonds. The force constants of the C—O bonds are close to those of C—C bonds and the masses of oxygen and carbon atoms are comparable. Consequently, the frequencies of C—O—C vibrations are close to frequencies of C—C vibrations. The C—O—C bands arise in the C—C skeletal vibrations region and the assignments, rendered more difficult, are not always characteristic. However, since the dipole-moment variations of the polar C—O bond are much larger than in C—C bonds, the $\nu\text{C—O}$ bands are stronger than $\nu\text{C—C}$ bands. The identification of ethers in the presence of other oxygenated organic compounds (alcohols, carbonyl compounds, acids, esters) is difficult and other regions of the spectrum must also be studied.

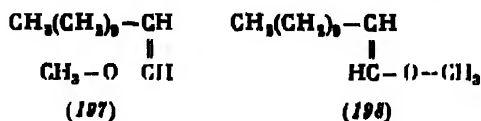
a. **Saturated aliphatic ethers.** The frequency of the asymmetrical stretching mode of the C—O—C bond in saturated aliphatic ethers is $1070\text{--}1150\text{ cm}^{-1}$ [67–69]. The symmetrical vibration occurs at a frequency of ca. 910 cm^{-1} .

Dimethyl ether in the vapor phase absorbs at 1122 and 940 cm^{-1} [70].

In spectra of higher members, the $\nu\text{C—O—C}$ absorptions lie in a broader region: $1070\text{--}1250\text{ cm}^{-1}$ [71].

b. **Unsaturated and aromatic ethers.** These compounds have in their structure the group $\text{C}=\text{C—OR}$. The frequency of the $=\text{C—O}$ group is higher than in aliphatic compounds and occurs in the range $1200\text{--}1260\text{ cm}^{-1}$ [69]. In a number of vinyl ethers $\text{CH}_2=\text{CH—OR}$, the asymmetrical vibration has frequencies in the range $1200\text{--}1275\text{ cm}^{-1}$ and the symmetrical vibration between 1020 and 1075 cm^{-1} [69]. The sym $\nu\text{C—O—C}$ band is weaker.

On comparing spectra of *cis* and *trans*-methyl-1-dodecenyl ethers, it has been observed that the *cis* isomer (197) absorbs at 1260 cm^{-1} and that its frequency is 60 cm^{-1} higher than in the *trans* isomer (198). The same difference has been observed in stereoisomers of methyl-1-decenyl ether [72].



The C=C stretching vibration in α , β -unsaturated ethers gives rise to stronger absorptions than in alkenes. *trans*-Isomers have lower C=C frequencies (1650 cm^{-1}) than *cis* isomers (1670 cm^{-1}).

In aromatic ethers the asymmetrical $\nu\text{C}-\text{O}-\text{C}$ absorption occurs at 1250 cm^{-1} and the symmetrical one, at $1020-1040\text{ cm}^{-1}$ [73]. These bands have relatively constant positions, even in more complicated ether molecules.

1. **O-CH₃ group.** Methyl ethers containing the O-CH₃ group have a strong absorption at 1110 cm^{-1} [72]. The frequencies of the CH₃ group are also characteristic. The frequency of the symmetrical stretching vibration (νCH_3 , sym) falls to $2815-2832\text{ cm}^{-1}$ when the O-CH₃ group is attached to an aliphatic group [74, 75], and to 2850 cm^{-1} in aromatic compounds [79]. The asymmetrical vibration has a frequency of $2970-2990\text{ cm}^{-1}$, which is not characteristic (the ethoxyl group O-C₂H₅ absorbs at the same frequency).

2. **O-C(CH₃)₃ group.** The skeletal vibration of the *tert*-butyl group in hydrocarbons absorbs at $720-770\text{ cm}^{-1}$. In $\text{O}-\text{C}(\text{CH}_3)_3$ the frequency rises to $820-920\text{ cm}^{-1}$ because of the vicinity of the electronegative oxygen atom [76].

c. **Cyclic ethers.** In cyclic ethers the vibrations of the C-O-C bond are not as distinct as in acyclic ethers. They are strongly coupled with vibrations of other ring atoms and are rather considered as vibrations of the whole ring system. In the corresponding region of the spectrum the pattern is dependent on the ring size [77].

1. **Cyclic ethers with three-membered rings (epoxides).** For the first member of this series, ethylene oxide, a complete vibrational analysis has been carried out [78]. Fundamental frequencies and vibration types are shown in Table II-95. Propylene oxide was also analyzed [80].

Table II-95 Frequencies and assignments in ethylene oxide [79]

| Assignment | Species | Frequency, cm^{-1} | Type of vibration |
|------------|---------|--------------------------------|--|
| ν_1 | A_1 | 3005 | C-H stretching (νCH) |
| ν_{13} | A_2 | 3063 | |
| ν_9 | B_1 | 3019 | |
| ν_{10} | B_2 | 3079 | |
| ν_8 | A_1 | 1490 | CH ₂ scissoring (δCH_2) |
| ν_7 | B_1 | 1470 | |
| ν_3 | A_1 | 1120 | CH ₂ out-of-plane wagging (δCH_2w) |
| ν_8 | B_1 | 1153 | |
| ν_{14} | A_2 | 1345 | CH ₂ out-of-plane twisting (δCH_2t) |
| ν_{11} | B_2 | 1143 | |
| ν_{15} | A_2 | 807 | CH ₂ in-plane rocking (γCH_2r) |
| ν_{13} | B_2 | 821 | |
| ν_6 | A_1 | 1266 | Ring (pulsation) |
| ν_5 | A_1 | 877 | Ring deformation |
| ν_6 | B_1 | 892 | |

The frequency of the C-H stretching vibration in epoxides is comparable to that of the C-H bond in cyclopropane. It occurs above 3000 cm^{-1} and is

characteristic for the strained three-membered ring. Depending on the degree of substitution of the epoxide ring, the frequencies are in the range 3000–3060 cm^{-1} . The band moves toward lower frequencies on increasing the degree of substitution. The vibration of the tertiary C–H bond in epoxides with straight chains (199) or in unstrained six-membered cyclic compounds (200) has a frequency of 3000 cm^{-1} [81]. In epoxides of five-membered cycloalkenes (201), the frequency rises to 3030–3040 cm^{-1} . In bridged bicyclic systems, the frequency corresponds to the size of the cycloalkane ring attached to the epoxide. The epoxide ring attached to the end of the chain and thus containing the CH_2 group (202) gives rise to the highest frequencies, 3040–3050 cm^{-1} , corresponding to the frequency in cyclopropane [74].

Substituted epoxides have three strong characteristic bands, at 750–1280 cm^{-1} assigned to ring vibrations: 750–875 cm^{-1} (12 μ), 810–950 cm^{-1} (11 μ), and 1230–1280 cm^{-1} (8 μ) [82–85] (Table II-96).

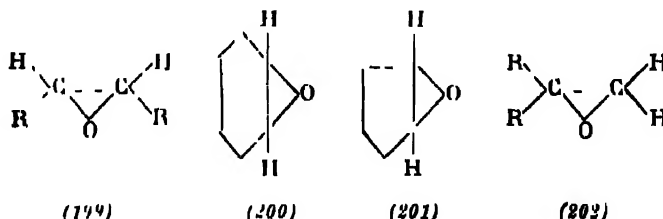


Table II-96 Characteristic frequencies in the 750–1250 cm^{-1} region [85]

| Epoxide | Frequency, cm^{-1} | | |
|-----------------|-----------------------------|---------|---------|
| Trisubstituted | 1235–1279 | 810–950 | 805–875 |
| Disubstituted | 1235–1280 | 810–950 | 775–875 |
| Monosubstituted | 1235–1280 | 810–950 | 750–770 |

Characteristic frequencies for a number of epoxides with characteristic structures are given in Table II-97.

Table II-97 Characteristic frequencies in epoxides [85]

| Epoxide | Frequency, cm^{-1} | | |
|-------------------------------------|-----------------------------|-----|-----|
| 2, 3-epoxy-2, 2, 4-trimethylpentane | 1266 | 811 | 751 |
| 1, 2-epoxy-2, 2, 4-trimethylpentane | 1253 | 881 | 792 |
| epoxycyclohexane | 1263 | 891 | 812 |
| 1, 2-epoxyoctane | 1253 | 919 | 834 |

The 1230–1280 cm^{-1} band (8 μ) is maintained (approximately constant) in all epoxides (Tables II-96 and II-97). In the 812–950 cm^{-1} (11 μ) the frequency is variable.

The 850 cm^{-1} band ($12\text{ }\mu$) is sensitive to structural changes. The following limits have been set for this absorption depending on substitution [85]:

trisubstituted compounds, $750\text{--}771\text{ cm}^{-1}$;
 disubstituted compounds, $775\text{--}847\text{ cm}^{-1}$;
 monosubstituted compounds, $806\text{--}877\text{ cm}^{-1}$.

2. *Four-membered cyclic ethers.* By analogy with other cyclic ethers the strong band at $970\text{--}980\text{ cm}^{-1}$ was assigned to the ring vibration [77, 86]. Sometimes the band occurs as a doublet with a strong component at $970\text{--}1000\text{ cm}^{-1}$ and a weaker one at $940\text{--}950\text{ cm}^{-1}$ [87]. In some compounds this doublet is accompanied by a band at ca. 900 cm^{-1} . It is of variable position [77, 78]. Other characteristic absorptions are those of CH_2 and CH_3 groups in substituted compounds. The deformation mode band δCH_2 occurs at $1200\text{--}1250\text{ cm}^{-1}$ (1250 cm^{-1} in trimethylene oxide) [77].

3. *Five- and six-membered cyclic ethers.* Studies connected with the furanose and pyranose structure of sugars prompted extensive investigations of five- and six-membered cyclic ethers [78].

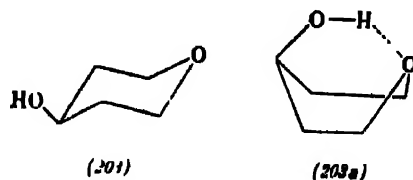
The planar or nonplanar conformation of tetrahydrofuran and deuterated tetrahydrofuran [88] was widely discussed [89–91]; the proposed assignments are slightly different [92].

In 2- and 2,5-alkylsubstituted compounds the absorption occurs at 1075 cm^{-1} [77, 93]. The frequency falls to 960 cm^{-1} in the tetrahydrofuran ring condensed with another ring. 3-Alkylfurans have also been investigated [94]. In six-membered cyclic ethers (tetrahydropyrans) the analysis of vibration modes has been carried out and assignments have been made for the chair form [89]. In six-membered hydroxy-ethers a hydrogen bond between the ring oxygen and the hydroxyl group may occur. The νOH frequency was used in assignments of conformations of some tetrahydropyrans and 1,3-dioxanols [95]. The observed νOH frequencies are shown in Table II-98.

Table II-98 νOH frequencies (cm^{-1}) in tetrahydropyrans and dioxanol [95]

| Compound | Free νOH | Bonded νOH |
|-----------------------------------|---------------------|-----------------------|
| 1, 4-tetrahydropyranol (203) | 3620 | — |
| 1, 3-tetrahydropyranol (204, 205) | 3620 | 3604 |
| 1, 3-dioxan-5-ol (206, 207) | 3635 | 3594 |

The absence of the intramolecularly bonded νOH band in 1, 4-tetrahydropyranol (Fig. II-76) is considered proof for the chair conformation (203) of the molecule. The formation of a hydrogen bridge would be possible only in a boat



conformation (203a) which is known to be thermodynamically unfavored. In this instance the energy provided by the formation of a hydrogen bond is not sufficient to convert the chair form into the boat form.

1, 3-Tetrahydropyranol shows both free OH and intramolecularly bonded OH absorptions. By analogy with cyclohexane, one would expect the OH group to be equatorial (204). However, this group can form an intramolecular hydrogen bond only in the axial position (205). The intensity of these bands

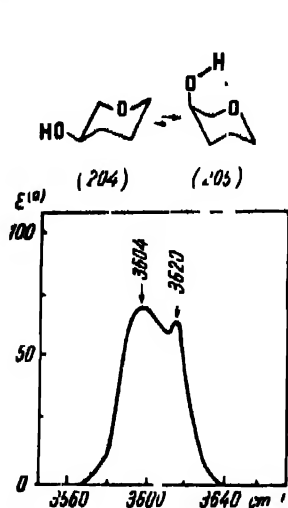


Fig. II-76 Infrared spectrum of 1,3-tetrahydropyranol in the vOH stretching mode region.

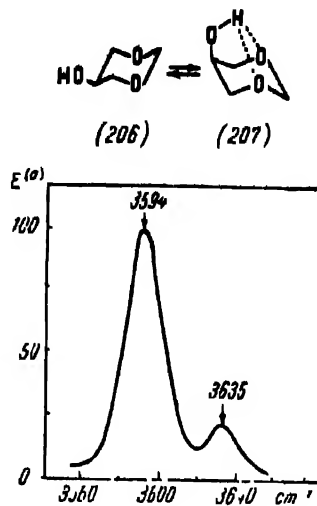
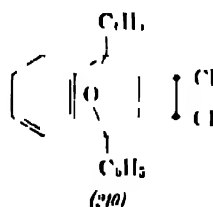
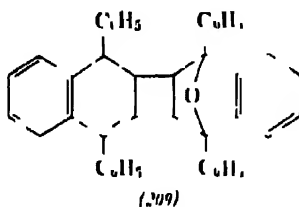
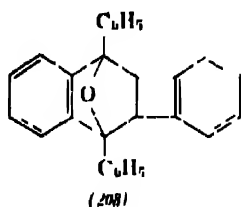


Fig. II-77 Infrared spectrum of 5-hydroxy 1,3-dioxan in the vOH stretching mode region

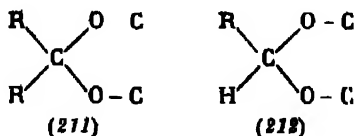
shows the existence of an equilibrium where OH equatorial and OH axial chair forms are present in a 1:1 ratio. Consequently, the energy of the hydrogen bond is sufficient to maintain the hydroxyl in the axial position. In 1, 3-dioxan-5-ol, the chair form with axial OH (207) is predominant (Fig. II-77 [95]).

4. *Bridged compounds.* In polycyclic compounds with oxygen bridges, the frequency of the C—O—C bond occurs at 990-1020 cm⁻¹.

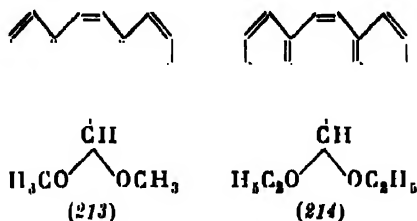
In a number of polycyclic compounds obtained by condensation of diphenylbenzofuran, the C—O—C absorption occurs at 1020 cm⁻¹ (208) [96], 990-1000 cm⁻¹ (209) [97], and 1010 cm⁻¹ (210).



5. *Ketals and acetals.* Infrared spectra of ketals and acetals (ethers with two alkoxy groups attached to the same carbon atom) show 4–5 bands between 1040 and 1200 cm^{-1} [98–100]. A number of simple ketals show four bands, at 1158–1190 cm^{-1} , 1124–1143 cm^{-1} , 1063–1098 cm^{-1} and 1038–1056 cm^{-1} , assigned to the coupled vibrations of C–O–C bonds (211). Acetals (212) have an additional band at 1105–1116 cm^{-1}



Cyclic ketals and spiroketals in sapogenins with a steroid skeleton show several bands between 650 and 1350 cm^{-1} [101, 102]. Dimethylacetal (213) absorbs at 1070, 1088, 1112, and 1125 cm^{-1} , and diethylacetal (214) absorbs at 1042, 1068, 1112, 1123, 1135, and 1168 cm^{-1} .



The frequency of C–O–C bonds in methyl glucosides (which can be considered particular cases) lies in the range 1070–1150 cm^{-1} .

b. Peroxides and hydroperoxides

These compounds do not have characteristic bands in the infrared because O–O bonds are involved in the vibrations of the molecular skeleton as a whole and are sensitive to any changes (substitutions) influencing the motions of the skeleton.

The weak band in the 820–890 cm^{-1} was tentatively assigned to the –O–O– vibrations in hydroperoxides [103, 101]; in peroxides this band occurs at ca. 1000 cm^{-1} .

The νOH absorption in hydroperoxides (3450 cm^{-1}) does not differ in shape or intensity from that in alcohols.

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CHAPTER 4

ORGANIC-SULFUR COMPOUNDS

Spectra of organo-sulfur compounds have been extensively studied [1]. However, group frequencies and correlations are less reliable than in other classes of compounds.

Bands arising from S—H linkages are weak, but they are well-defined and can be readily identified. Vibrations of S=O bonds give rise to strong characteristic absorptions. Their frequencies vary with the oxidation state of the sulfur atom and the nature of substituents. For example, SO, SO₂, and SO₃ groups can be readily distinguished. Variations due to substituents are not large enough to enable accurate¹ correlations. By comparing the S=O with the C=O group, useful indications have been obtained in establishing factors influencing the force constant in both cases.

Simple C—S and S—S bonds give rise to weak absorptions of variable frequency and of reduced value in structural analysis.

a. Thioalcohols, thiophenols, and thioacids

a. **S—H bond.** The S—H bond occurring in mercaptans and thiophenols had been recognized in infrared spectra at an early date [2–4]. The 2550–2600 cm⁻¹ band was assigned to this vibration [1, 3]. Band position in this region depends on the nature of the group attached to the S—H group.

Alkylmercaptans absorb at the upper limit of the region, thiophenols in the middle, and thioacids have the lowest frequency. The bands are weak (ca. 1/10 as compared to OH vibrations) [5]. No hydrogen bonds have been observed between alkylmercaptans [6, 7]. The frequency does not vary with aggregation state. It is the same in the gaseous and the liquid phase, or in solution [3]. The association of the SH group in mercaptans with N, S, O atoms does not result in shifts larger than 10–20 cm⁻¹ [8]. Thiophenols associate with pyridine, picoline, or sulfoxides. In these cases the decrease in frequency is substantial [9, 10].

Frequencies of bonded ν SH and ν OH bands and $\Delta\nu$ shifts in mixtures of thiophenols with various sulfoxides are shown in Table II-99.

Table II-99 ν SH and ν OH frequencies (cm⁻¹) in mixtures of sulfoxides with thiophenols and phenols

| Sulfoxide | + Thiophenol | | + Phenol | |
|----------------------|--------------|-------------|----------|-------------|
| | ν SH | $\Delta\nu$ | ν OH | $\Delta\nu$ |
| Diethylsulfoxide | 2488 | 97 | 3235 | 385 |
| Ethylphenylsulfoxide | 2515 | 70 | 3285 | 335 |
| Diphenylsulfoxide | 2537 | 48 | 3320 | 300 |

It can be seen that the shift in thiophenol mixed with dialkylsulfoxides is ca. 100 cm⁻¹. It falls to 70 cm⁻¹ in mixtures with phenylalkylsulfoxides and to 48 cm⁻¹ in diarylsulfoxides. The strong bonding in sulfoxides, cf. the carbonyl group in ketones, cannot be explained solely by the greater polarity of the S—O bond [1]. Thioacetic acid is not bonded and the value of the ν SH frequency is the same in the vapor phase, the liquid phase, or in solution. Dithioacetic acid, however, is bonded. The ν SH frequency falls by 80 cm⁻¹

in going from the vapor to the liquid state [11]. The SH group forms strong bonds with P=S and C=S bonds. The shifts are as large as 140 cm^{-1} [12].

The SH absorption is weak, and in dilute solutions, it is sometimes difficult to recognize. In compounds with COOH groups, the band is overlapped by the carboxyl absorption in this region.

Conformation studies have shown that ethanedithiol $\text{HSCH}_2\text{CH}_2\text{SH}$ in the solid state has a *trans* conformation. In solution, staggered *anti* and *syn* conformations are in equilibrium, as in the case of dichloroethane. In dialkylthioethanes the amount of *anti* form increases with the volume of the substituent [13].

b. C—S bond. The bands arising from C—S linkages occur at $600\text{--}700\text{ cm}^{-1}$. They are weak and of variable position [14]. In aromatic compounds the identification is difficult due to out-of-plane CH deformation modes of the aromatic ring occurring in this region [7]. Methylmercaptan absorbs at 705 cm^{-1} and ethylmercaptan, at 660 cm^{-1} . In higher members the assignments are uncertain and may be used only comparatively in the same homologous series.

Comparative studies of infrared and Raman spectra of many thioalcohols, thioethers, and disulfides enabled a classification of absorptions based on the nature of the alkyl group attached to sulfur. The frequency decreases in the order mercaptans > thioethers > disulfides [7]. In mercaptans the frequency decreases in the order primary > secondary > tertiary alkyl, and shifts from values mentioned below do not exceed 10 cm^{-1} in a great number of compounds.

| | | cm^{-1} |
|-----------------|--------------------------|------------------|
| Primary alkyl | $\text{CH}_3\text{—S—}$ | 685—705 |
| | $\text{RCH}_2\text{—S—}$ | 630—660 |
| Secondary alkyl | $\text{R}_2\text{CH—S—}$ | 600—630 |
| Tertiary alkyl | $\text{R}_3\text{C—S—}$ | 570—600 |

Cyclohexane derivatives do not fit this classification.

In unsaturated compounds with α , β -double bonds, the decrease in frequency is ca. 60 cm^{-1} , and an increase in band intensity is observed.

c. S—S bond. The S—S bond has a weak absorption in the infrared and a strong absorption in Raman [14]. In alkyldisulfides $\text{CH}_3\text{—S—S—CH}_3$ or $\text{C}_2\text{H}_5\text{—S—S—CH}_3$, it is assigned a weak band at $450\text{--}550\text{ cm}^{-1}$ [1] and in the dicyclohexyl derivative, at 510 cm^{-1} [7]. In aromatic disulfides, a weak band occurs at $430\text{--}490\text{ cm}^{-1}$ [15]. These bands do not have analytical value.

b. Thioketones. Thioamides

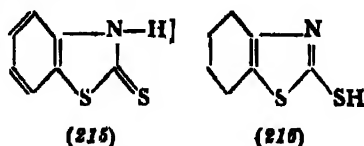
The C=S bond in thioketones cannot be as easily identified as the C=O bond in ketones.

In simple dialkylthioketones, the C=S vibration bands could not be identified [7]. This is understandable because thioketones undergo polymerization very readily, yielding trimers [16].

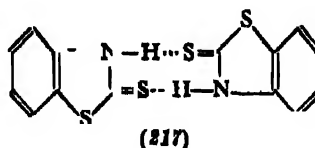
In thiobenzophenone $C_6H_5-CS-C_6H_5$, where the reactivity of the $C=S$ group is low, the monomeric form gives rise to a $C=S$ absorption at 1667 cm^{-1} [1].

In thioamides the $C=S$ bond occurs in the range $1000-1400\text{ cm}^{-1}$, depending on structure [1]. Thioacetamide $CH_3-CS-NH_2$ absorbs at 1310 cm^{-1} and thiocaprolactam, at 1117 cm^{-1} . The low frequency suggests a large contribution from the polar structure $\overset{+}{N}=C-\overset{-}{S}$. A band at 1480 cm^{-1} was also assigned to this structure [17]. Some authors assign to the $C-N$ vibration a band at 1300 cm^{-1} , implying strong double bond character for the $C=N$ bond and, consequently, a low frequency for the $C-S$ linkage.

The thione-thiol tautomerism has been proved by the isolation of N-alkyl and S-alkyl derivatives [18].



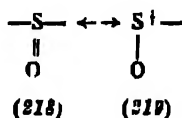
Infrared spectra do not prove the existence of structures (215) and (216) because NH and SH absorptions do not occur. This was explained by the formation of hydrogen bonds between SH and NH groups, yielding dimers (217) [1, 19]



c. Sulfoxides

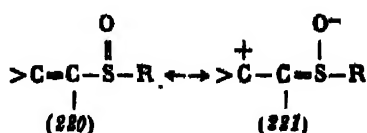
Sulfoxides are an intermediate state of oxidation between thioethers $R-S-R$ and sulfones $R-SO_2-R$.

The electronic structure of the sulfur-oxygen bond can be represented by (218) and (219) [20]



Structure (218) with a $S=O$ double bond is favored by electron attracting substituents [20, 21]. The frequency of the $S-O$ stretching vibration is directly dependent on the electronegativity of the substituent attached to the $S-O$ group.

It has been shown that the $C-S$ bond in diarylsulfoxides is 0.06\AA shorter than in dialkylsulfoxides. This implies a certain amount of double bond character due to resonance between structures (220) and (221).



In inert solvents (CCl_4), sulfoxides show a strong band at $1050 \pm 5 \text{ cm}^{-1}$ [19]. By comparison with the fundamental frequency in sulfur monoxide (1124 cm^{-1}) [22], this band undoubtedly corresponds to the $\text{S}=\text{O}$ stretching mode. The frequency is remarkably constant in sulfoxides where R is alkyl, cycloalkyl, aryl, and allyl (Table II-100) [15, 19, 23].

Table II-100 $\nu\text{S}=\text{O}$ frequencies (cm^{-1}) in sulfoxides [15,19,22]

| Sulfoxide | Solution in CCl_4 | Solid | Liquid |
|---------------------------|-------------------------------|-------|--------|
| Dimethylsulfoxide | 1055 | — | — |
| Diisobutylsulfoxide | 1040 | 1019 | — |
| Cyclohexylmethylsulfoxide | 1055 | — | 1040 |
| Phenylmethylsulfoxide | 1055 | 1035 | 1042 |
| Diphenylsulfoxide | 1055 | 1035 | 1044 |
| Diallylsulfoxide | 1047 | — | 1047 |
| Methylmethallylsulfoxide | 1061 | — | 1061 |

In going from the solid to the liquid state, or to dilute solutions in nonpolar solvents, shifts are ca. $10-20 \text{ cm}^{-1}$ [1, 24].

Larger shifts toward lower frequencies take place in protic solvents, such as thiophenols or even CHCl_3 , which form a bond with the polar $\text{S}=\text{O}$ linkage [1, 23].

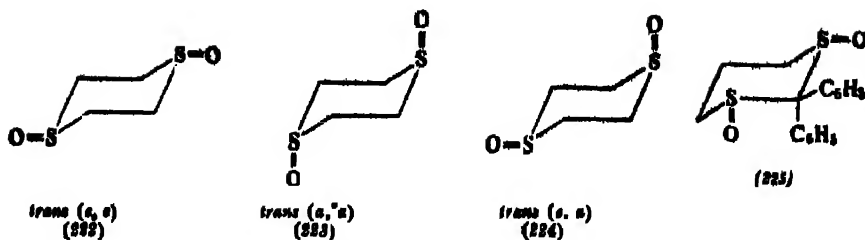
As opposed to carbonyl compounds, unsaturation or the presence of an aromatic ring adjacent to the $\text{S}=\text{O}$ group does not lower the frequency. This is because the substituent is not coplanar with the $\text{S}=\text{O}$ group and consequently there is no normal conjugation with π -electrons like in carbonyl compounds. However, ultraviolet spectra [25] and intensity measurements in the infrared [26] show that some conjugation does take place.

In six-membered cyclic sulfoxides, by analogy with the chair form of cyclohexane, axial and equatorial conformations can be distinguished (222)–(224).

In 1,1-dithiane-1, 4-dioxide the $\nu\text{S}=\text{O}$ frequency of the equatorial conformer is higher than that of the axial (see ϵ and a bands in cyclohexanols).

It is believed that α -1,4-dithiane-1,4-dioxide has a diaxial configuration (223) with a frequency of 1020 cm^{-1} . The equatorial $\text{S}=\text{O}$ group absorbs at $1032-1047 \text{ cm}^{-1}$.

The β -form of this compound is believed to have an ϵ , a conformation (224) [27].



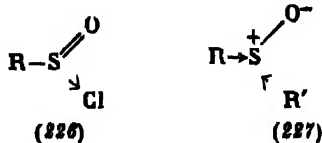
2,2-Diphenyl-1,3-dithiane-1,3-dioxide (225) has the equatorial $\text{S}=\text{O}$ frequency at 1085 cm^{-1} and the axial at 1060 cm^{-1} [28].

d. Sulfinic acids and derivatives

Sulfinic acids $\text{R}-\text{SO}-\text{OH}$ have a strong band at 1090 cm^{-1} [29].

a. **Sulfinic esters.** In esters $\text{R}-\text{SO}-\text{OR}'$ the frequency is higher than in the free acid. In these compounds the absorption at 1130 cm^{-1} is assigned to the $\text{S}=\text{O}$ group.

b. **Sulfinyl chlorides $\text{R}-\text{SO}-\text{Cl}$.** By attaching an electronegative chlorine atom to the sulfur atom, the frequency rises by ca. 60 cm^{-1} , cf. acids, reaching 1150 cm^{-1} [29]. The $-I$ effect of chlorine can be seen by comparison with sulfoxides (227) (1050 cm^{-1}) where $\text{R}' = \text{alkyl}$ ($+I$ effect). In chlorides, structure (226) has a greater contribution than the dipolar structure (227) in sulfoxides.



c. **Sulfinate ion.** The ion RSO_2^- has two bands, 1020 cm^{-1} and 980 cm^{-1} [29]. The fall in frequency and the doubling of the band in the sulfinate anion, cf. the free acid, may be explained by an internal conjugation (by analogy with the carboxylate anion RCOO^-).

e. Sulfurous acid derivatives

a. **Sulfites.** These esters have an $\text{S}=\text{O}$ group attached to two oxygen atoms (with a $-I$ effect), resulting in a rise in frequency, cf. sulfinic acid derivatives.

1. **Alkyl sulfites.** The first member of the series, dimethylsulfite has a slightly higher frequency, 1213 cm^{-1} (according to some authors [31] 1120 cm^{-1}), cf. the normal absorption of the $\text{S}=\text{O}$ group ($1200 \pm 5\text{ cm}^{-1}$) [30].

In $\text{C}_6\text{H}_5-\text{O}-\text{SO}-\text{O}-\text{C}_6\text{H}_5$ the phenyl group raises the $\text{S}=\text{O}$ frequency to 1245 cm^{-1} (Table II-101).

Table II-101 $\nu_{S=O}$ Frequencies (cm^{-1}) in sulfoxes RO-SO-OR' [30]

| R | R' | $\nu_{S=O}$ (in CCl_4) |
|--------------------------|--------------------------|----------------------------------|
| CH_3 | CH_3 | 1213, 1208 (1220, 1205)* |
| C_2H_5 | C_2H_5 | 1205 |
| CH_3 | C_2H_5 | 1205 |
| C_2H_5 | C_2H_5 | 1202 |
| $i\text{-C}_4\text{H}_9$ | $i\text{-C}_4\text{H}_9$ | 1203, 1200 |
| C_6H_5 | C_6H_5 | 1198 |
| C_6H_5 | C_6H_5 | 1245 |

* According to [31].

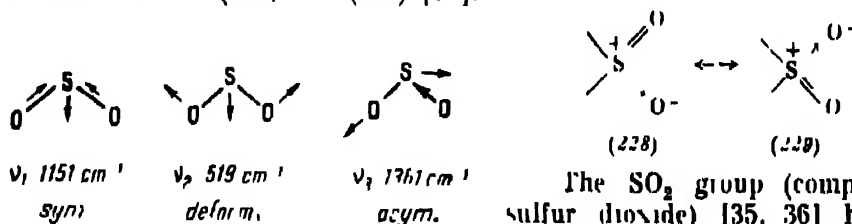
2. **Cyclic sulfites.** Cyclic sulfites (dithiolanes) absorb between 1210 and 1220 cm^{-1} [28, 30]. Differences between five-, six-, and seven-membered ring sulfites are not greater than a couple of cm^{-1} . There are indications that five-membered ring 1,3-disulfites have a slightly higher frequency than other cyclic sulfites [27, 32].

The constant value of the S—O frequency in smaller rings shows that in these systems the strain is partitioned between other bonds in the ring, leaving the $> \text{S}=\text{O}$ angle practically unchanged [1].

b. **Halides.** Thionyl chloride with two chlorine atoms attached to the $\text{S}=\text{O}$ group has a frequency of 1231 cm^{-1} [30]. In thionyl fluoride SOF_2 the more electronegative fluorine atom favors the structure with the S—O double bond and the frequency rises to 1320 cm^{-1} [30, 33].

f. Sulfones

Sulfones have an SO_2 group attached to two hydrocarbon groups. The widely discussed sulfonyl group SO_2 has an electronic structure intermediate between (228) and (229) [31].

Fig. II-78 Normal vibration modes of the SO_2 group

The SO_2 group (compared to sulfur dioxide) [35, 36] has two strong bands corresponding to symmetrical (ν_1) and asymmetrical (ν_3) vibration modes [19, 37, 37a] (Fig. II-78).

The $1140\text{--}1160\text{ cm}^{-1}$ band is assigned to the symmetrical mode and the $1300\text{--}1350\text{ cm}^{-1}$ band to the asymmetrical mode [37] (Table II-102). In sulfur dioxide the frequencies of the two vibrations are 1151 and 1361 cm^{-1} [36]. It was shown that a linear relationship exists between $\nu_{\text{SO}_2, \text{ asym}}$ and $\nu_{\text{SO}_2, \text{ sym}}$ [38, 39].

Table 11-103 νSO_2 frequencies (cm^{-1}) in Sulfones

| Sulfone | νSO_2 , sym | | | νSO_2 , asym | | |
|-------------------|------------------------------------|--------|-------|------------------------------------|--------|-------|
| | Solu- tion in CCl_4 | Liquid | Solid | Solu- tion in CCl_4 | Liquid | Solid |
| Cyclohexylmethyl- | 1144 | 1138 | | 1321 | 1309 | — |
| Dicyclohexyl- | 1130 | | 1124 | 1312 | — | 1299 |
| Phenylmethyl- | 1160 | 1155 | 1150 | 1334 | 1318 | 1293 |
| Diphenyl- | 1164 | | 1151 | 1336 | — | 1313 |
| Methylallyl- | 1130 | | | 1307 | — | — |
| Methylvinyl- | 1139 | — | | 1312 | — | — |
| Phenylvinyl- | 1153 | — | — | 1325 | — | — |

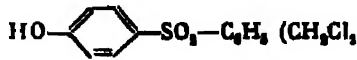
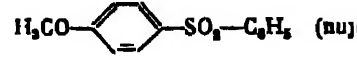
In solution sulfones absorb at higher frequencies (by 10–20 cm^{-1}) than in the solid state [19, 28].

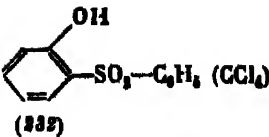
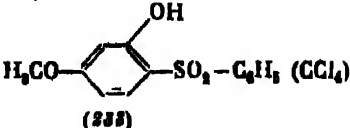
The symmetrical vibration band in diphenylsulfone occurs at 1164 cm^{-1} in carbon tetrachloride and at 1151 cm^{-1} in the crystalline state. The asymmetrical vibration band occurs at 1336 cm^{-1} in CCl_4 and at 1313 cm^{-1} in the solid state.

In a number of cyclic disulfones [28], the SO_2 symmetrical vibration occurs at 1133–1156 cm^{-1} in chloroform and at 1129–1149 cm^{-1} in the solid state. The νSO_2 asym band occurs at 1316–1353 cm^{-1} in chloroform and at 1285–1339 cm^{-1} in the solid state. In this case differences do not exceed 10 cm^{-1} .

In aromatic disulfones frequencies and band intensities are slightly higher than in aliphatic sulfones (1155–1165 cm^{-1}). Some authors [26] believe that this is due to conjugation between the SO_2 group and the aromatic ring. Other papers do not support this view [19, 40, 41]. However, the SO_2 group has a strong influence on the $\text{C}=\text{C}$ double bond [40] (see below).

It is observed that in hydroxydiphenylsulfones with the OH group in the *ortho* position to the SO_2 group, the frequency of the νSO_2 sym vibration is lower. In para-substituted compounds this frequency occurs at 1150 cm^{-1} . The OH frequency decreases also, which points to a weak intramolecular bonding [42]. Frequency variations (cm^{-1}) in the following compounds are meaningful.

| | νSO_2 | free νOH | bonded νOH |
|--|------------------|---------------------|-----------------------|
|  (130) | 1151 | 3590 | 3383 |
|  (221) | 1150 | — | — |

| | νSO_2 | free νOH | bonded νOH |
|--|------------------|---------------------|-----------------------|
|  (332) | 1138 | — | 3292 |
|  (333) | 1130 | — | 3292 |

g. Sulfonic acids and derivatives

a. **Halides.** The electronegative halogen atom raises the frequency of the SO_2 group in $-\text{SO}_2\text{X}$. In sulfochlorides the νSO_2 sym frequency occurs at $1170 \pm 5 \text{ cm}^{-1}$ and νSO_2 asym at $1370 \pm 3 \text{ cm}^{-1}$. In benzenesulfochloride the νSO_2 sym frequency is slightly higher (1185 cm^{-1}) and the νSO_2 asym frequency slightly lower (1340 cm^{-1}) (Table II-103).

Table II-103 νSO_2 frequencies (cm^{-1}) in sulfonic acid halides

| Halide | νSO_2 | | References |
|---|------------------|------|------------|
| | Sym | Asym | |
| $\text{CH}_3\text{SO}_2\text{Cl}$ | 1175 | 1372 | [43] |
| $\text{C}_6\text{H}_5-\text{SO}_2\text{Cl}$ | 1165 | 1367 | [31] |
| $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ | 1185 | 1340 | [37] |
| $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$ | 1166 | 1366 | [37] |
| $\text{ClO}_2\text{S}(\text{CH}_2)_n\text{SO}_2\text{Cl}$ | 1162 | 1359 | [44] |
| $\text{Cl}_2\text{CSO}_2\text{Cl}$ | 1183 | 1404 | [45] |
| $\text{CH}_3\text{SO}_2\text{I}$ | 1220 | 1449 | [45] |
| SO_2Cl_2 | 1205 | 1437 | [45] |
| SO_2F_2 | 1269 | 1502 | [45] |

The frequency increases in α -halosulfonyl halides [45]. The more powerful $-I$ effect of the fluorine atom results in larger shifts toward higher frequencies. Methanesulfofluoride absorbs at 1220 and 1449 cm^{-1} [1, 45]. The extreme case is sulfuryl fluoride with νSO_2 asym at 1502 cm^{-1} and νSO_2 sym at 1269 cm^{-1} (see halides of carboxylic and carbonic acids).

b. **Sulfonamides** $\text{R}-\text{SO}_2-\text{NH}_2$. Sulfonamides have strong absorptions at $1160\text{--}1180 \text{ cm}^{-1}$ and $1330\text{--}1360 \text{ cm}^{-1}$ assigned to the two vibrations of the SO_2 group. The symmetrical vibration frequency varies from the solid state to solution. The asymmetrical vibration frequency falls by $10\text{--}20 \text{ cm}^{-1}$ [1, 46]. Both frequencies are higher than in sulfones (contrary to the shift direction in amides).

c. **Sulfonic esters** $\text{R}-\text{SO}_2-\text{OR}'$. The symmetrical νSO_2 vibration gives rise to a strong absorption in the range $1145\text{--}1200 \text{ cm}^{-1}$ and the asymmetrical vibration, between $1330\text{--}1420 \text{ cm}^{-1}$ [31, 44, 47] (Table II-104).

Table II-104 νSO_2 frequencies (cm^{-1}) in sulfonic esters

| Compound | νSO_2 | | References |
|---|------------------|------------|------------|
| | Sym | Asym | |
| $\text{CH}_3\text{CH}_2\text{SO}_2\text{OCH}_3$ | 1176 | 1351, 1370 | [31] |
| $\text{CH}_3\text{CH}_2\text{SO}_2\text{OC}_2\text{H}_5$ | 1176 | 1351, 1370 | [31] |
| $\text{CH}_3\text{OOC}_2\text{SCH}_2\text{CH}_2\text{SO}_2\text{OCH}_3$ | 1158 | 1347 | [44] |
| $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OR}$ | 1170–1192 | 1350–1375 | [47] |

d. **Sulfonic acids and salts** RSO_3H and RSO_3^- . Few papers deal with infrared spectra of sulfonic acids. For identification purposes the following bands have been proposed: 1150–1260 cm^{-1} , 1010–1080 cm^{-1} and 600–700 cm^{-1} [48].

Table II-105 νSO_2 frequencies (cm^{-1}) in sulphonie acids and salts

| Compound | νSO_2 | | Compound | νSO_2 | |
|--|------------------|------|--|------------------|------|
| | Sym | Asym | | Sym | Asym |
| $\text{CH}_3\text{SO}_3\text{H}$ | 1059 | 1190 | $\text{CH}_3(\text{CH}_2)_2\text{SO}_3\text{Na}$ | 1044 | 1176 |
| $\text{CF}_3\text{SO}_3\text{H}$ | 1031 | 1274 | $\text{CH}_3(\text{CH}_2)_2\text{SO}_3\text{Na}$ | 1044 | 1172 |
| $\text{CH}_3\text{SO}_3\text{Na}$ | 1053 | 1195 | $(\text{CH}_3)_2(\text{SO}_3\text{Na})_2$ | 1046 | 1200 |
| $\text{CF}_3\text{SO}_3\text{Na}$ | 1042 | 1279 | $(\text{CH}_3)_2(\text{SO}_3\text{K})_2$ | 1041 | 1205 |
| $\text{CH}_3(\text{SO}_3\text{Na})_2$ | 1042 | 1183 | $(\text{CH}_3)_2(\text{SO}_3)_2\text{Ca}$ | 1050 | 1190 |
| $\text{CH}_3\text{CH}_2\text{SO}_3\text{Na}$ | 1053 | 1176 | $(\text{CH}_3)_2(\text{SO}_3\text{NH}_4)_2$ | 1037 | 1190 |
| $\text{CH}_3(\text{CH}_2)_2\text{SO}_3\text{Na}$ | 1048 | 1182 | | | |

Table II-105 shows the sym νSO_2 and asym νSO_2 vibrations for a number of monosulfonic acids and salts [49], and disulfonic acids and salts [44].

h. *The influence of the sulfur atom on the vibrations of neighboring bonds in the hydrocarbon radical*

a. **C—H bond.** Frequencies arising from stretching vibrations of CH_3 and CH_2 groups attached to the sulfur atom do not shift significantly as to be of use for identification. The asymmetrical stretching mode of the CH_3 group has a frequency of 2960–2969 cm^{-1} . In ethylsulfate the frequency is 2970–2980 cm^{-1} . The frequency of the symmetrical vibration is 2880 cm^{-1} for the CH_3 group and 2861 cm^{-1} for CH_2 .

Band intensities are slightly higher than in hydrocarbons. The symmetrical deformation mode of the CH_3 group attached to sulfur falls to ca. 1320 cm^{-1} , i. e., by about 60 cm^{-1} , cf. the $\text{H}_3\text{C—C}$ frequency in hydrocarbons [1, 50–52]. The absorptions occur at 1335 cm^{-1} in CH_3SH , 1309 and 1334 cm^{-1} in CH_3SCH_3 , 1323 cm^{-1} in $\text{CH}_3\text{SC}_2\text{H}_5$, 1315 cm^{-1} in $\text{CH}_3\text{SCH}(\text{CH}_3)_2$, and 1316 cm^{-1} in $\text{CH}_3\text{SC}(\text{CH}_3)_3$. Branched chains have two absorptions, but only the first one is characteristic [1, 52]. In the $(\text{CH}_3)_2\text{CHS}$ group, the absorption occurs at 1365 and 1380 cm^{-1} and in $(\text{CH}_3)_2\text{CS}$, at 1365 and 1390 cm^{-1} .

Deformation vibrations of the CH_3 group occur at 1450 cm^{-1} in compounds containing the $\text{CH}_3\text{CH}_2\text{S}$ group. In most cases the band is indistinguishable from that of the asymmetrical vibration of the CH_3 group. When bands can be distinguished, the lower frequency band is assigned to the CH_3 deformation mode and the higher frequency band to the CH_3 asym deformation mode [1].

Strong absorptions arise between 900 and 1100 cm^{-1} . They were assigned to other vibration modes of various sulfur compounds [1, 51].

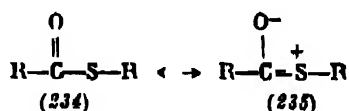
b. **C=C bond.** The C=C absorption occurs at ca. 1580 cm^{-1} , appreciably lower than the normal frequency, even in conjugated double bonds [1]. Not enough data is available to assess it as a general phenomenon.

The $=\text{C}-\text{H}$ deformation frequency does not seem to be affected by the sulfur atom.

c. **C=N bond.** The C=N bond attached to sulfur through the carbon atom has been studied for a variety of compounds without internal conjugation [53]. In thiooximes the absorption occurs at 1620 cm^{-1} , much lower than in oximes ($1640-1690\text{ cm}^{-1}$).

Compounds with a conjugated C=N bond absorb at lower frequency and the presence of a neighboring sulfur atom lowers it further still. According to some authors [53], the interaction of the sulfur atom with π -electrons of the C=N group is greater than in the case of oxygen or nitrogen atoms.

d. **C=O bond.** The most interesting interactions occur in the carbonyl group. Thioesters $\text{R}-\text{CO}-\text{SR}$ have the $\nu\text{C}=\text{O}$ frequency at $1680 \pm 10\text{ cm}^{-1}$. The low frequency as compared to carboxylic esters shows an appreciable contribution of structure (235).



The same effect is observed in thioacetic acid CH_3COSH and in thio-lactones. It is interesting that in this system α , β -unsaturation and the presence of atoms with a $-I$ effect ($-\text{CF}_3$) do not alter the C=O frequency, cf. carboxylic acids and their derivatives [54, 55]. It is believed that the increase in frequency due to the s -cis conformation (with F next to O) is cancelled by the interaction of fluorine and sulfur atoms. This results in a greater positive charge on sulfur and a decrease in the C=O bond order (236).



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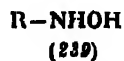
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CHAPTER 5

ORGANIC NITROGEN COMPOUNDS

Organic nitrogen compounds can formally be considered as derivatives of inorganic compounds. Nitro- (237) and nitrosoderivatives (238) are obtained from nitric and nitrous acid, respectively, by substitution of the hydroxyl group with organic groups, and hydroxylamine derivatives (239) are obtained by substitution of one or several of the hydrogen atoms of hydroxylamine with organic groups.



Similarly, primary (240) secondary (241), and tertiary amines (242) result from ammonia.

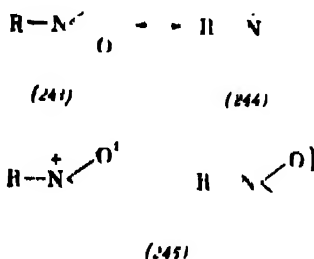


Some compounds with functional groups containing two nitrogen atoms can be considered as derivatives of hydrazine $\text{H}_2\text{N-NH}_2$, while others (e.g. azo compounds) cannot be derived from any inorganic substance.

Infrared spectra of organic nitrogen compounds are described according to the above classification [1].

A. NITROCOMPOUNDS

The structure of the nitro group was established by measurements of interatomic distances (electron diffraction and X-ray analysis have shown that the two oxygen atoms are equidistant from the nitrogen atom (1.22Å)) and by dipole moment measurements (zero for *p*-dinitrobenzene) which show that the two π electrons are equally distributed between the two NO bonds by isovalent conjugation. The uniform π electron distribution in the NO₂ group can be represented by formula (245) expressing an intermediate situation between (243) and (244)[1].



The vibrational behavior of the nitro group (Fig II-79) fully supports this structure. The characteristic absorptions arising from symmetrical and asymmetrical stretching modes occur in the expected regions (1275–1375 cm⁻¹ and 1535–1620 cm⁻¹, respectively.)

Characteristic frequencies in nitromethane are shown in Table II-106.

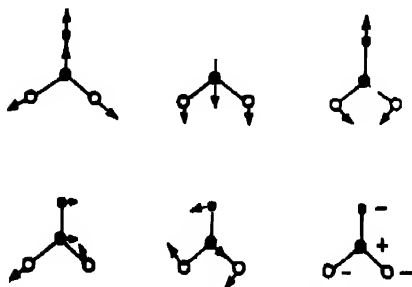


Fig. II-79 Normal vibration modes of the C-NO₂ group:

• -carbon atom; ● -nitrogen atom; ○ -oxygen atom.

Table II-106 Fundamental frequencies in nitromethane

| Vibrational type | Frequency cm ⁻¹ | Vibrational type | Frequency cm ⁻¹ |
|-----------------------|----------------------------|---------------------|----------------------------|
| νNO_2 asym | 1587 | δNO_2 | 656 |
| νNO_2 sym | 1370 | γNO_2 | 615 |
| νCN | 917 | δCNO | 482 |

For identification purposes only, νNO_2 and, to a lesser extent, νCN vibrations are of value. Bands arising from deformation modes are difficult to distinguish from other bands occurring in the low frequency region.

a. Saturated nitro compounds

Characteristic absorptions of nitroalkanes occur at $1368\text{--}1370\text{ cm}^{-1}$ (νNO_2 sym) and $1550\text{--}1567\text{ cm}^{-1}$ (νNO_2 asym) [2-5a]. In primary nitroalkanes these frequencies do not change with chain length. The differences noticed between absorptions of primary and secondary derivatives are not large enough for identification purposes. Generally, primary derivatives RCH_2NO_2 have higher frequencies than secondary ones, R_2CHNO_2 . Tertiary nitrocompounds R_3CNO_2 have the lowest frequency ($1342\text{--}1358$ and $1530\text{--}1545\text{ cm}^{-1}$). They can be distinguished from primary and secondary compounds (see Table II-107). Bands occurring at ca. 1536 cm^{-1} are considered characteristic form tertiary derivatives and at ca. 1550 cm^{-1} for primary and secondary nitrocompounds [4].

Table II-107 Characteristic mean frequencies in nitro compounds cm^{-1} [1-3]

| Compound | νNO_2 asym | νNO_2 sym | $\nu\text{C--N}$ |
|---|-----------------------|----------------------|------------------|
| <i>Nitroalkanes</i> | | | |
| CH_3NO_2 | 1567 | 1379 | 917 |
| $\text{CH}_3\text{CH}_2\text{NO}_2$ | 1550 | 1302 | 874 |
| RCH_2NO_2 | 1555 | 1375 | 876 |
| R_2CHNO_2 | 1553 | 1301 | 851 |
| R_3CNO_2 | 1536 | 1350 | - |
| <i>Nitr ohaloalkanes</i> | | | |
| RCH(X)NO_2 (X= Cl, Br) | 1575 | 1348 | 848 |
| $\text{R}_2\text{C(X)NO}_2$ (X= Cl, Br) | 1565 | 1342 | - |
| $\text{R}_3\text{C(X)NO}_2$ (X= Cl) | 1567 | 1332 | - |
| Cl_3CNO_2 | 1610 | 1307 | 842 |
| Br_3CNO_2 | 1592 | 1305 | 840 |
| F_3CNO_2 | 1610 | 1307 | - |
| $\text{F}_2\text{ClC--CF}_2\text{NO}_2$ | 1618 | 1274 | 909 |
| <i>Dinitroalkanes</i> | | | |
| $\text{RCH(NO}_2)_2$ | 1582 | 1333 | - |
| $\text{R}_2\text{C(NO}_2)_2$ | 1572 | 1326 | - |
| <i>Nitrocycloalkanes</i> | 1538 1548 | 1357 1377 | |

1. *Nitrocycloalkanes*. νNO_2 absorptions of these compounds correspond to those of secondary or tertiary nitro derivatives of straight-chain alkanes [2, 4]. Nitrocyclohexane absorbs at 1548 and 1377 cm^{-1} . In three-membered rings the frequency falls. 1-Methylnitrocyclopropane absorbs at 1538 and 1357 cm^{-1} . The decrease in frequency is due to the cyclopropane ring, unsaturated in nature, also noticed in other cases [3]. In nitro compounds substituted in the α -position with electronegative atoms or groups with $-I$ effect, the fre-

quency of the asymmetrical stretching mode increases and that of the symmetrical mode decreases [3].

2. *Dinitro derivatives.* Dinitro compounds with the two nitro groups attached to the same carbon atom absorb at ca. 1580 cm^{-1} (νNO_2 , asym) and 1330 cm^{-1} (νNO_2 , sym). The increase in frequency of the asymmetrical vibration and the decrease of the symmetrical one is because of the $-I$ effect of the second NO_2 group. In many instances bands arising from the symmetrical vibration in *gem*-dinitro compounds are split. In tetranitromethane both absorptions are doubled [2].

b. α -Halonitroalkanes.

The presence of one or several halogen atoms in the position alpha to the NO_2 group results in an increase in frequency of the asymmetrical vibration and a decrease in frequency of the symmetrical νNO_2 mode. The bands shift in both directions by about the same number of cm^{-1} . Shifts increase with the number of halogen atoms (see Table II-107). They are ca. 20 cm^{-1} for one chlorine atom, ca. 32 cm^{-1} for two chlorine atoms, and still larger for three chlorine atoms; for example, chloropicrine absorbs at 1610 and 1307 cm^{-1} [6]. A small decrease in frequency is observed in $\text{Br}_3\text{C}-\text{NO}_2$, cf. $\text{Cl}_3\text{C}-\text{NO}_2$. Surprisingly, the frequency in CF_3-NO_2 is relatively low [5,6].

c. Nitroesters

The negative effect of the $-\text{COOR}$ group in nitroesters results in small shifts in frequency of the two stretching vibrations of the NO_2 group [3,4]. On the average the shifts are of the order of 10 cm^{-1} . The frequency of the $\text{C}=\text{O}$ group is shifted toward higher values. A characteristic absorption in α -nitro esters is that of the CH_2 group in the α -position, occurring at 1430 cm^{-1} .

Vibrations of the alkyl radical. In primary nitroalkanes the sym νNO_2 absorption is sometimes accompanied by a band at 1429 cm^{-1} [2,3]. It is assigned to the deformation mode of the CH_2 group adjacent to the NO_2 group. These absorptions, along with the absorption occurring at 1560 cm^{-1} , are characteristic for primary nitro compounds [2].

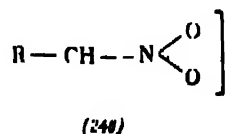
In general the frequency of the symmetrical deformation mode of the methyl group coincides with the symmetrical stretching mode of the NO_2 group. However, if the CH_3 and NO_2 groups are attached to the same carbon atom (in structures such as $\text{CH}_3-\text{C}-\text{NO}_2$), the two bands are well separated, occurring at 1395 and 1370 cm^{-1} , respectively. Compounds with two methyl groups attached to the carbon bearing the NO_2 group ($(\text{CH}_3)_2\text{CX}-\text{NO}_2$) show bands at $(400, 1375, 1350, \text{ and } 855\text{ cm}^{-1})$. They seem to be characteristic for this structure and are not affected by the nature of mass of the substituent X (Table II-108).

Table 11-108 Characteristic absorptions in $(\text{CH}_3)_2\text{CX-NO}_2$ [2]

| X | Frequency, cm^{-1} | | | |
|---------------------------|-----------------------------|------|------------|----------|
| H | 1401 | 1374 | 1361 | 850 |
| CH_3 | 1404 | 1372 | 1346 | 857 |
| CH_2CH_3 | 1397 | 1372 | 1353 | 856 |
| CH_2OCH_3 | 1401 | 1376 | 1353 | 850 |
| CH_2NO_2 | 1399 | 1374 | 1346 | 861 |
| C_6H_5 | 1399 | 1376 | 1351 | 851 |
| Cl | 1397 | 1377 | 1342 | 848 |
| NO_2 | 1406 | 1377 | 1357, 1330 | 855, 845 |

d. *aci-Nitrocompounds*

In sodium salts of primary and secondary nitrocompounds, the mesomeric ion (246) shows absorptions of the $\text{C}=\text{N}$ bond at ca. 1600 cm^{-1} , while characteristic absorptions of the NO_2 group disappear. The sodium salt of



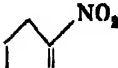

nitromethane absorbs at $1580 \pm 2\text{ cm}^{-1}$ [7,8] and that of 2-nitropropane, at 1608 cm^{-1} [7].

In sodium salts of nitropropane, butane, pentane, and hexane, two bands are assigned to the $\nu\text{C}=\text{N}$ vibration: a very strong one occurring at 1600 cm^{-1} and a weak one at 1660 cm^{-1} . The second band is supposed to arise from an isomerism which is not very likely in such ions [9]. In solid state the $=\text{NOO}^-$ group gives rise to strong absorptions (doublets) at $1277-1262\text{ cm}^{-1}$ and $1018-1033\text{ cm}^{-1}$. In aqueous solution, single bands arise at 1253 and 1012 cm^{-1} [8]. In sodium salts of other nitrocompounds a strong, broad absorption between 1166 and 1178 cm^{-1} is assigned to this vibration [9].

e. *Nitroalkenes*

In α , β -unsaturated nitrocompounds with the NO_2 group directly attached to the double bond, the νNO_2 frequency decreases. In mono-, di-, and trisubstituted nitroalkenes, the frequency decreases slightly with increasing number of alkyl substituents. Monoalkyl derivatives absorb at $1524 \pm 4\text{ cm}^{-1}$ and $1353 \pm 6\text{ cm}^{-1}$, and di- and trisubstituted compounds at 1515 ± 4 and $1346 \pm 9\text{ cm}^{-1}$ [2,10].

In the four nitrobutenes (247)–(250) variations in frequency with structure can be clearly seen [2.]

| | | | |
|---|--|---|---|
| | $\begin{array}{c} \text{CH}_2-\text{C}=\text{CH}-\text{CH}_2 \\ \quad \\ \text{NO}_2 \quad \text{CH}_3 \end{array}$ | $\begin{array}{c} \text{CH}=\text{C}-\text{CH}_2-\text{CH}_2 \\ \quad \\ \text{NO}_2 \quad \text{CH}_3 \end{array}$ | $\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{CH}-\text{CH}_2 \\ \quad \\ \text{H}_2\text{C} \quad \text{NO}_2 \end{array}$ |
| νNO_2 asym, cm^{-1} | 1555 | 1548 | 1520 |
| νNO_2 sym, cm^{-1} | 1376 | 1359 | 1346 |
| | (247) | (248) | (249) |
| | $\begin{array}{c} \text{H}_3\text{C}-\text{C}=\text{C}-\text{CH}_2 \\ \quad \\ \text{H}_3\text{C} \quad \text{NO}_2 \end{array}$ |  |  |
| νNO_2 asym, cm^{-1} | 1515 | 1513 | 1550 |
| νNO_2 sym, cm^{-1} | 1340 | 1337 | 1363 |
| | (250) | (251) | (252) |

The influence of the NO_2 group on $\nu\text{C}=\text{C}$ and δCH frequencies is small. However, the $\nu\text{C}=\text{C}$ band becomes stronger. The δCH band intensity increases when the NO_2 group is attached to the same carbon atom as the alkene hydrogen ($=\text{CH}-\text{NO}_2$). Table II-109 shows the characteristic frequencies of nitroalkenes, cf. the corresponding alkenes ($\text{R}-\text{alkyl}$).

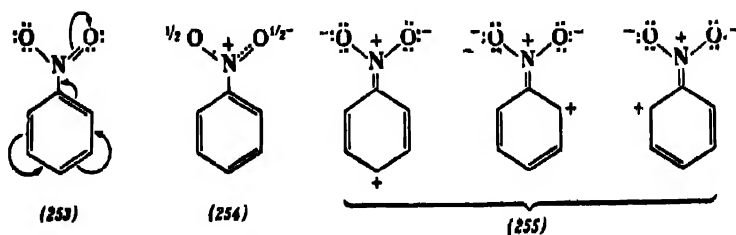
Table II-109 Characteristic frequencies in nitroalkenes [2]

| Nitroalkene | Substituent λ | $\nu\text{C}=\text{C}$ | $\delta\text{C} \quad \text{H}$ |
|---|--------------------------|------------------------|---------------------------------|
| $\text{CH}_2=\text{CH}-\lambda$ | R | 1642-1647 | 925-1000 |
| | CNO_2 | 1617 | 916-991 |
| | NO_2 | 1612 | 940-965 |
| $\lambda-\text{CH}=\text{CH}-\lambda(\text{trans})$ | R | | 963-978 |
| | R, CNO_2 | 1664-1678 | 962-969 |
| | R, NO_2 | 1650-1656 | 957-961 |
| $\lambda-\text{CH}=\text{CH}-\lambda(\text{cis})$ | R | 1650-1656 | 666 |
| | R, CNO_2 | 1661 | 666 |
| $\lambda_2\text{C}=\text{CH}_2$ | R | 1639-1661 | 888-892 |
| | R, CNO_2 | 1650-1660 | 909-923 |
| | R, NO_2 | 1667-1675 | 937-942 |
| $\lambda_2\text{C}=\text{CHX}$ | R | 1631-1667 | 800-833 |
| | R, CNO_2 | 1631-1658 | 800-833 |
| | R, NO_2 | 1631-1661 | 823-836 |
| $\lambda_2\text{C}=\text{CX}_2$ | R | — | — |
| | R, CNO_2 | 1672 | — |
| | R, NO_2 | 1664 | — |

f. Aromatic nitrocompounds

Frequencies of NO_2 stretching vibrations in aromatic nitrocompounds are lower than those in nitroalkanes. Monocyclic aromatic nitrocompounds absorb at $1490-1570 \text{ cm}^{-1}$ (νNO_2 asym) and $1300-1370 \text{ cm}^{-1}$ (νNO_2 sym) [2, 11-15].

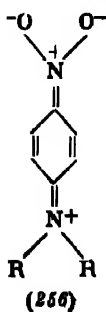
Nitrobenzene absorbs at 1530 and 1353 cm^{-1} [2,14]. Changes in physical state and nature of the solvent result in much smaller frequency shifts than in other compounds substituted with polar groups [2].



The decrease in νNO_2 frequency in aromatic nitro compounds, cf. aliphatic nitro compounds, is due to conjugation of the NO_2 group with the aromatic ring. In nitrobenzene (253) conjugation results in a much larger contribution of structures (255) than of structure (254). The N—O bond order (and frequency) decrease and the C—N bond order (and frequency) increase.

In substituted nitrobenzene the νNO_2 frequency varies with position, number, and nature of substituents. However, variations are different for the two vibration modes [2,3,14]. The influence is stronger on the asymmetrical νNO_2 vibration.

In *para*-disubstituted compounds, the νNO_2 asym band occurs at 1490—1565 cm^{-1} [13, 14]. Electron-releasing substituents shift the frequency toward the lower limit and electron-attracting substituents (groups with $-I$ or $-E$ effects) shift the frequency towards the upper limit (Table II-110). The largest decrease in frequency is observed in the case of NH_2 and NR_2 substituents (*p*-nitroaniline, 1504 cm^{-1}) with the strongest $+E$ effect. In these compounds the contribution of structure (256) is the largest. Decrease in the $+E$ effect (OH , OCH_3) results in lower frequencies. In the case of substituents with $-I$ and $-E$ effects (NO_2), the frequency increases because of an increase in N—O bond order, determined by a decrease in electron density at the nitrogen atom of the NO_2 group [2,3,14]. Halogen atoms with a strong $-I$ effect and a $+E$ effect give intermediate values. The larger contribution of the more polar structure (256) results in an increase in the dipole moment of the molecule. A linear relationship was found between the νNO_2 asym frequency and the dipole moment of the NO_2 group [13]. In *para*-disubstituted compounds the same parallelism exists between the νNO_2 asym frequency and the σ -Hammett constant of substituents [13, 14].



The νNO_2 asym frequency decreases with substituents with more negative values and rises for positive values (Table II-110).

Table II-110 νNO_2 frequencies (cm^{-1}) in $\text{X}-\text{C}_6\text{H}_4-\text{NO}_2$

| X | νNO_2 , asym | νNO_2 , sym | Hammett constant σ [16] | Constant σ' [17] |
|---------------------------|-------------------------|------------------------|--------------------------------|-------------------------|
| $\text{N}(\text{CH}_3)_2$ | 1489 | 1316 | -0.600 | -0.972 |
| NH_2 | 1504 | 1333 | -0.660 | |
| OH | 1515 | 1342 | -0.357 | |
| OCH_3 | 1517 | 1342 | -0.268 | |
| CH_3 | 1517 | 1344 | -0.170 | |
| NHCOCH_3 | 1515 | 1335 | -0.015 | |
| Cl | 1526 | 1343 | +0.227 | |
| Br | 1532 | 1345 | +0.232 | |
| I | 1513 | 1345 | +0.276 | |
| COOCH_3 | 1535 | 1348 | +0.522 | +0.636 |
| COOH | 1541 | 1351 | +0.265 | +0.728 |
| CN | 1524 | 1348 | +0.628 | +1.000 |
| NO_2 | 1560 | 1344 | +0.778 | +1.27 |
| H | 1530 | 1350 | +0.000 | |

The frequency of the symmetrical νNO_2 vibration lies in the range 1300–1350 cm^{-1} . The influence of *para*-substituents on this vibration is more complex [2].

The intensity of νNO_2 bands varies independently of Hammett- σ values; however, a decrease in intensity of the νNO_2 asym and a rise in intensity of the νNO_2 sym absorption is observed for more negative σ values [2].

As expected, in *meta*-disubstituted compounds changes in νNO_2 asym frequency are smaller. A small decrease in frequency (ca. 10 cm^{-1} cf. nitrobenzene) is observed for the NH_2 group (nitroaniline absorbs at 1520 cm^{-1}), while the NO_2 group raises the frequency by the same amount (1410 cm^{-1} in *m*-dinitrobenzene). The effect is stronger in 1,3,5-trinitrobenzene absorbing at 1548 cm^{-1} [11].

In *ortho*-disubstituted compounds the interactions between the two groups are more complicated [4]. In addition to the conjugative effect there is a field effect working in the opposite direction. νNO_2 asym frequencies for a number of substituted nitrobenzenes are shown in Table II-111 (in CCl_4 , KBr , and CHBr_3) [11].

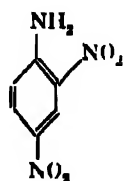
Table II-111 νNO_2 asym frequencies in substituted nitrobenzene

| Compound | Substituent position | <i>Ortho</i> | | <i>Meta</i> | | <i>Para</i> |
|------------------------------------|----------------------|--------------|----------------|-----------------|--------------|--------------|
| | | KBr | CCl_4 | CHBr_3 | KBr | KBr |
| Nitro- <i>N,N</i> -dimethylaniline | | | 1521 s | | 1530 s | 1489 m |
| Nitroaniline | | 1512 s | | 1511 s | 1520 s | 1508 m |
| Nitroanisole | | | 1529 s | | 1531 s | 1501 s |
| Nitrophenol | | 1530 s | | 1534 s | 1526 s | 1500 s |
| Dinitrobenzene | | 1530 s | | 1545 s | 1540 s | 1563 s |
| | | 1545 w | | | | |

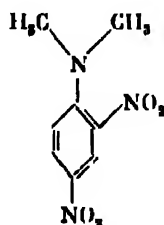
As in the case of *para*-disubstituted compounds, a decrease in frequency is observed in substituents with a more negative Hammett- σ constant favoring *ortho*-quinoid structures.

In compounds where for steric reasons the two groups are out of the plane of the ring, conjugation is prevented and the νNO_2 asym frequency rises, reaching the values observed in aliphatic compounds. In *o*-dinitrobenzene (KBr) two bands occur: 1530 and 1545 cm^{-1} (shoulder). They cannot be explained by a vibrational coupling [14]. In sterically hindered *o*-nitrodimethylaniline the frequency (1521 cm^{-1}) is lower than expected. This is thought to be due to intramolecular interactions between the two *ortho*-substituents by analogy with *o*-nitrophenol where the chelate hydrogen bond does not change the νNO_2 frequency but produces a large decrease in the νOH frequency (to 3240 cm^{-1}). In *m*- and *p*-nitrophenol the free νOH frequency is 3390 cm^{-1} . In nitroaniline the two νNH_2 bands occur at normal positions: νNH_2 asym at 3470 cm^{-1} and νNH_2 sym at 3360 cm^{-1} .

Substituted polynitro compounds show a larger number of νNO_2 asym bands, which enable some interesting tentative assignments [14]; for example, 2,4-dinitroaniline (257) shows two bands: 1524 cm^{-1} corresponding to the NO_2 group in the *ortho*-position and 1498 cm^{-1} , corresponding to the conjugated NO_2 group in the *para*-position. 2,4-Dinitro-*N,N*-dimethylaniline (258) shows three bands: 1510, 1515, and 1498 cm^{-1} . The 1498 cm^{-1} band was assigned to the NO_2 group in the *para*-position (conjugated with the NR_2 group coplanar with the benzene ring) (259). In this structure the *ortho*- NO_2 group is out of plane and absorbs at 1510 cm^{-1} . Also, another band arises at 1515 cm^{-1}



(257)

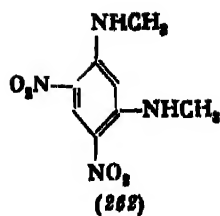
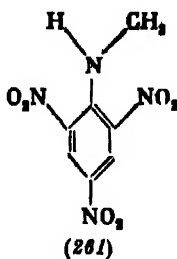
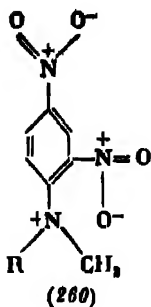
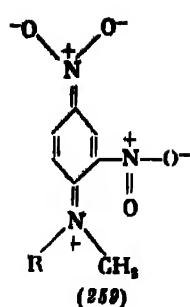


(258)

assigned, as in *o*-nitrodimethylaniline to structure (260) where the *ortho*- NO_2 group is coplanar with the NR_2 group. Thus the infrared spectrum points out the coexistence of the two structures (259) and (260).

In 2,4,6-trinitro-*N*-methylaniline (261), conjugation is precluded and the absorptions occur at 1532 cm^{-1} (*p*- NO_2) and 1516 cm^{-1} (*o*- NO_2). The conjugated *p*- NO_2 band in the 1490 cm^{-1} region is absent.

In 1,3-bis-methylamino-1,6-dinitrobenzene (262), the NO_2 groups (conjugated because of steric reasons) absorb at 1510 cm^{-1} [14].

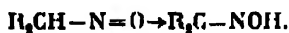
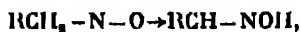


Vibrations of the C—N bond. The C—N vibration in nitroalkanes was associated with a medium intensity band in the range $830\text{--}920\text{ cm}^{-1}$ [3]. In aromatic compounds conjugation increases the C—N bond order [2, 12, 13]. The absorption occurring at ca. 860 cm^{-1} was assigned to this vibration. In nitrobenzenes substituted in the *para* position with electron-donating groups the increase in C—N bond order is followed by a decrease in the N—O bond order. The total effect results in a stabilization of the C—N vibration [19].

Comparison of infrared spectra of nitrobenzene and perdeuteronitrobenzene has shown that the only bands which are unaffected by deuteration are those at 850 and 1300 cm^{-1} . The 850 cm^{-1} band is superimposed on the CH deformation vibrations of the aromatic ring. Since the C—N bond order in aromatic compounds is larger than in aliphatic compounds, it is conceivable that the absorption occurring at 1300 cm^{-1} arises from the C—NO₂ bond [2].

B. NITROSO COMPOUNDS

The direct determination of the N=O frequency in nitroso compounds is possible in only a few cases. Primary and secondary nitroso compounds readily undergo isomerization to the corresponding oximes:



Consequently, special precautions have to be taken on recording infrared spectra of these compounds. The majority of tertiary aliphatic nitroso compounds exist under normal conditions in the form of dimers. A great number of older assignments where this fact has not been taken into account are erroneous.

Spectra of unstable primary and secondary nitroso compounds are recorded in special cells heated to $100\text{--}200^\circ\text{C}$. The recording has to be done rapidly (within five minutes at the most) [19].

The isomerization of the sample can be followed by observing the disappearance of bands characteristic for the nitroso form and the appearance of bands arising from the corresponding oxime. It was shown that nitroso-

methane absorbs at 1564 cm^{-1} ($\nu\text{N}=\text{O}$). The band disappears after a few minutes and bands arising from formaldoxime can be observed. Freshly prepared nitrosocyclohexane shows $\nu\text{N}=\text{O}$ bands at 1558 cm^{-1} and CH_2 bands at 2857 and 2933 cm^{-1} . The intensity of these bands decreases rapidly. They disappear completely after a few minutes and new absorptions belonging to

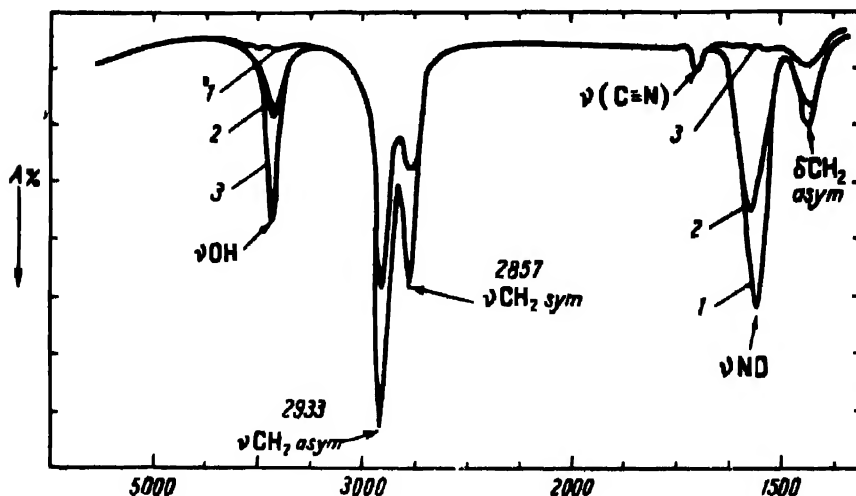


Fig. 11-80 Infrared spectrum of secondary nitroso compounds.

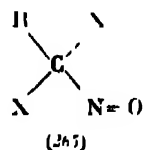
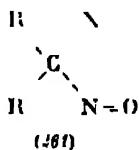
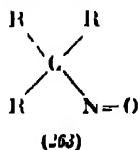
(1) Freshly prepared nitrosocyclohexane; (2) after 5 minutes; (3) after 15 minutes.

cyclohexanone oxime occur at 3636 cm^{-1} (νOH) and 1653 cm^{-1} ($\nu\text{C}=\text{N}$) (Fig. 11-80).

The same technique is used in recording spectra of nitroso derivatives obtained by depolymerization of dimers [19].

N—O stretching vibration. The N—O bond in stable nitroso compounds (tertiary aliphatic and aromatic) is characterized by a stretching vibration in the range $1488\text{--}1621\text{ cm}^{-1}$. The wide range and the low frequency of this vibration must be pointed out, cf. other double bonds, $\text{C}=\text{C}$, $\text{C}=\text{N}$, and $\text{C}=\text{O}$.

Nitrosoalkanes. In solution tertiary nitrosoalkanes (263) show absorptions at $1555 \pm 9\text{ cm}^{-1}$. In the vapor phase the frequency rises by ca. 10 cm^{-1} . If the carbon atom bearing the N—O group is attached to an element other than carbon, shifts in frequency due to the electronic effect of the respective group are observed.



In nitroso compounds with a chlorine atom, or a CN, or an NO_2 group in the α -position ($-I$ effect) (264), the frequency rises to $1580 \pm 10\text{ cm}^{-1}$.

Two or three halogen atom (265) increase the frequency still further. Vapors of 2,2-dichloronitrosoethane $\text{CH}_3\text{CCl}_2-\text{N}=\text{O}$ absorb at 1598 cm^{-1} and $\text{Cl}_2\text{C}-\text{N}=\text{O}$, at 1621 cm^{-1} [20]. The trifluoro derivative $\text{F}_3\text{C}-\text{N}=\text{O}$ absorbs at 1595 cm^{-1} [21]. 1-Nitroso-1-chlorocyclohexane (solution) absorbs at 1558 cm^{-1} and 1,4-dichloro-1,4-dinitrosocyclohexane, at 1557 cm^{-1} [22]. On substitution with acetyl groups, the frequency falls to 1539 cm^{-1} . Substituents in the β -position do not affect the vibration of the NO group.

In asymmetrically substituted compounds (in solution), a splitting of the band into two components $10\text{--}20\text{ cm}^{-1}$ apart is observed. In the vapor phase a broadening of the band takes place. This behavior is attributed to conformational isomers arising from restricted rotation about the C-N bond [20, 23].

Aromatic nitroso compounds. In these compounds the frequency is lower than in nitrosoalkanes or nitrosocycloalkanes. It lies in the range $1488\text{--}1513\text{ cm}^{-1}$ [19]. In solution nitrosobenzene absorbs at 1506 cm^{-1} and α -nitrosonaphthol, at 1508 cm^{-1} . The frequency is sensitive to the nature and position of substituents in the aromatic ring. νNO frequencies for a number of nitrosobenzenes substituted in the *para*-position with electron-attracting and electron-donating groups are shown in Table II-112.

Table II-112 νNO frequencies (monomers) in *para*-substituted nitrosobenzenes

| $\text{X}-\text{C}_6\text{H}_4-\text{N}=\text{O}$ X= | $\nu\text{N}=\text{O}\text{ cm}^{-1}$ |
|---|---------------------------------------|
| NO_2 | 1513 |
| F | 1511 |
| CH_3 | 1508 |
| H | 1506 |
| OCH_3 | 1497 |
| Br | 1497 |
| I | 1488 |

Electron-donating substituents (OCH_3 , I) reduce the frequency, and electron-attracting substituents (NO_2) raise the frequency.

Substitution in the *meta*-position does not affect the frequency, cf. $\text{C}_6\text{H}_5\text{NO}$; *ortho*-disubstituted compounds have normal frequencies.

νNO frequencies in dimers of nitroso compounds $(\text{R}-\text{NO})_2$. In spectra of dimers the $\text{N}=\text{O}$ band in the $1488\text{--}1598\text{ cm}^{-1}$ region disappears and a new strong band of lower frequency appears in the range $1176\text{--}1430\text{ cm}^{-1}$ [24]. Extensive studies of many dimeric aliphatic and aromatic nitroso derivatives have shown that the two monomeric molecules are linked through nitrogen atoms. In such a structure the oxygen atoms is bonded in the same manner as in aminoxides or *N*-oxides of heterocyclic compounds. The low frequency is in line with a polarized N-O bond. The $\text{N}=\text{N}$ double bond makes *cis-trans* isomerism possible. The centrosymmetric *trans* forms (266) have a single $\text{N}=\text{O}$ absorption in this region. *Cis* forms (267) have two bands (Table II-113).

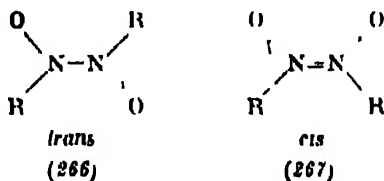


Table II-113 Characteristic frequencies in *cis* and *trans* dimers of nitroso compounds

| R | <i>trans</i> form | <i>cis</i> form |
|-----------|---|--|
| Aliphatic | A single band 1176–1290 cm^{-1} | Two bands (a) 1323–1344 <i>m</i> (b) 1387–1426 <i>vs</i> |
| Aromatic | A single band 1253–1299 cm^{-1} | Two bands (a) 1389 or 1397 <i>vs</i> (b) 1409 <i>vs</i> |

In the *trans*-aliphatic series the first member (the dimer of nitrosomethane) has an abnormal frequency, at 1290 cm^{-1} . In dimers $(\text{CH}_3)_2\text{C}(\text{X})\text{N}=\text{O}$, where $\text{X}=\text{NO}_2$, CN , CH_3 , CH_2Cl , COCH_3 , the frequencies lie in the range 1236–1297 cm^{-1} . In branched-chain or cyclic compounds the frequency decreases to 1183–1222 cm^{-1} . The smallest value occurs in phenylnitrosomethane (1176 cm^{-1} .)

In the aromatic *trans* series, frequencies are more constant. It should be pointed out that the frequency in aryl- NO_2 (ca. 1250 cm^{-1}) is analogous to that of pyridine-*N*-oxides (1212 cm^{-1}). In nitrosobenzene or substituted in *para*-position with halogens (F, Cl, Br), CH_3 , OCH_3 , NO_2 , CHO groups, the frequency lies in the range 1252–1259 cm^{-1} . *p*-Nitrosobenzoic acid and 2,4,6-tribromonitrosobenzene have a higher frequency (1285 and 1289 cm^{-1} , respectively).

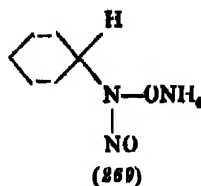
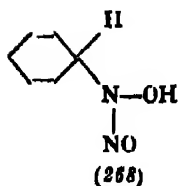
Infrared spectroscopy has shown that the majority of nitroso compounds obtained by normal synthetic procedures belong to the *trans* series [24a]. However, nitrosomethane ($\nu\text{NO}=1399$ and 1342 cm^{-1}) and 1-chloro-1-nitrosocyclohexane (1399 and 1350 cm^{-1}) belong to the *cis* series. In the aromatic series only nitrosobenzene (1409 and 1397 cm^{-1}) and α -nitrosonaphthalene (1409 and 1389 cm^{-1}) have a *cis* conformation. Nitrosobenzene bands show dichroism [25].

C. ORGANIC DERIVATIVES OF HYDROXYLAMINE

Compounds RNHONH have not been extensively studied.

The characteristic absorption of the N–O bond in hydroxylamine H_2NOH occurs at 894 cm^{-1} [26].

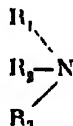
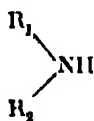
Alkylhydroxylamines have strong absorptions at 869 cm^{-1} [27]. The νNH band occurs at lower frequencies (ca. 3250 cm^{-1}) than in amines [27, 28]. *N*-Nitrosocyclohexyl hydroxylamine (268) shows two absorptions, 3330 cm^{-1} (νOH) and 1105 cm^{-1} . In the ammonium salt (269) they are replaced by bands at 3077 and 1385 cm^{-1} (KBr) [29].



D. AMINES

Primary and secondary amines can be identified in the infrared spectrum by the vibrations of NH_2 and NH groups, analogous to characteristic vibrations of CH_2 and CH groups in hydrocarbons. However, the electronegative character of the nitrogen atom makes this bond more polar and the presence of mobile unshared electrons enables the variation of the force constant with structure.

In the $\text{N}-\text{H}$ stretching mode region ($3050-3500\text{ cm}^{-1}$) primary amines show two bands and secondary amines show a single band. Not having a hydrogen atom attached to nitrogen, tertiary amines absorb in this region [30, 31].



NH bonds in amines share some common properties with the OH group. Because of this sometimes the absorptions arising from these two groups are superimposed precluding their identification. Since nitrogen is less electronegative than oxygen the $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds are weaker, and frequency shifts away from normal values are smaller (100 cm^{-1} at the most). (These shifts are only slightly larger than those that occur by modification of the physical state of the sample.) νNH frequencies are lower than νOH frequencies. In dilute solutions the vibrations of the two (free) groups can be readily distinguished. In concentrated solutions their modification is more difficult. Hydrogen bonded amides also absorb in this region. Figure II-81 shows the infrared spectrum of aniline in the $3000-3600\text{ cm}^{-1}$ region in dilute carbon tetrachloride solution; the sharp bands of the NH_2 vibration can be observed.

a. $\text{N}-\text{H}$ stretching vibration.

1. *Primary amines.* The two stretching modes of the NH_2 group give rise to two bands between 3300 and 3500 cm^{-1} .

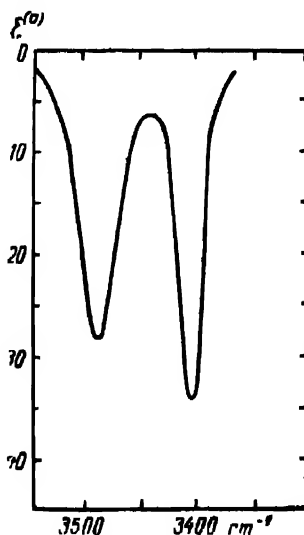
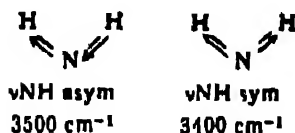


Fig. II-81 Infrared spectrum of aniline in the $\text{N}-\text{H}$ stretching mode region.



The higher frequency band at ca. 3500 cm^{-1} (Fig. II-81) corresponds to the asymmetric mode and the band at ca. 3400 cm^{-1} arises from the symmetric mode. The following empirical relationship exists between the two modes:

$$\nu\text{ sym} = 345.5 + 0.876 \nu\text{ asym (cm}^{-1}\text{)}.$$

The observed differences do not exceed 4.8 cm^{-1} [32].

The frequency of the NH_2 vibrations depends on the nature of the hydrocarbon group R.

Aliphatic amines have lower frequencies and weaker absorptions than aromatic amines (Table II-114).

Table II-114 νNH_2 frequencies in primary amines [33]

| Amine | Solution in CCl_4 | | Vapor phase | |
|-------------------------|----------------------------|------------------|-------------------|------------------|
| | $\nu\text{ asym}$ | $\nu\text{ sym}$ | $\nu\text{ asym}$ | $\nu\text{ sym}$ |
| Methylamine | 3398 | 3311 | 3425 | 3360 |
| n-Propylamine | 3390 | 3322 | 3410 | 3342 |
| Isopropylamine | 3383 | 3319 | 3434 | 3332 |
| n-Butylamine | 3387 | 3324 | 3412 | 3348 |
| Aniline | 3481 | 3394 | 3407 | 3416 |
| α -Naphthylamine | 3472 | 3390 | 3478 | 3401 |
| β -Naphthylamine | 3475 | 3390 | 3484 | 3407 |

Except for the first member of the series, methylamine, which has a higher frequency, all the other members of the aliphatic primary amines series show the two absorptions (in solution) at $3387 \pm 5\text{ cm}^{-1}$ and $3322 \pm 5\text{ cm}^{-1}$. In the vapor phase the two absorptions occur at $3425 \pm 15\text{ cm}^{-1}$ and $3340 \pm 10\text{ cm}^{-1}$. Aromatic primary amines absorb at higher frequencies. In solution the bands occur at $3476 \pm 5\text{ cm}^{-1}$ and $3391 \pm 5\text{ cm}^{-1}$, and in the vapor phase, at $3487 \pm 10\text{ cm}^{-1}$ and $3408 \pm 10\text{ cm}^{-1}$.

The rise in NH frequency observed in aromatic amines is characteristic for the NH_2 group. This behavior is different from that of the OH group or of other groups conjugated with the aromatic ring. Both groups (OH and NH_2) have identical electronic effects ($-I$ and $+E$) and are involved in conjugation, giving rise to structures such as (270) and (271), in which the nitrogen and oxygen atoms become more positive. Therefore similar variation in force constants of NH and OH bonds could be anticipated. Indeed, in phenol electronic effects produce a decrease in force constant (in phenols the νOH vibration has a lower frequency than in alcohols) (Table II-115). In amines the electronic effect is shielded by a hybridization effect. In aliphatic amines the

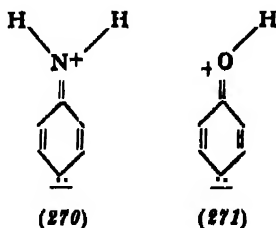
nitrogen atom with a pyramidal configuration has an almost sp^3 hybridization. The force constant is influenced by adjacent atoms or groups in the same way as in alcohols. However, in aromatic amines the nitrogen atom is partially rehybridized toward sp^2 due to conjugation. This increases the s -char-

Table II-116 Force constants of O-H and N-H bonds [34]

| O-H Bond | $k \cdot 10^{-3}$ dyn/cm | N-H Bond | $k \cdot 10^{-3}$ dyn/cm |
|------------------|-----------------------------|--|-----------------------------|
| H_2O | 7.70 | NH_3 | 6.38 |
| CH_3OH | 7.54 | CH_3NH_2 | 6.40 |
| C_6H_5OH | 7.36 | $(CH_3)_3NH$ | 6.31 |
| $n-C_6H_5OH$ | 7.35 | $H_2C \begin{array}{c} \diagup \quad \diagdown \\ NH \end{array} CH_2$ | 6.08 |
| $(CH_3)_3C-OH$ | 7.26 | $C_6H_5NH_2$ | 6.54 |
| $C_6H_5CH_2OH$ | 7.27 | $(C_6H_5)_3NH$ | 6.55 |
| C_6H_5OH | 7.25 | $CH_3C_6H_4NH_2$ | 6.50 |
| $(C_6H_5)_2CHOH$ | 7.26 | $CH_3O-C_6H_4NH_2$ | 6.45 |
| $(C_6H_5)_2COH$ | 7.25 | | |

acter of the N-H bond. The bond becomes stronger, and the frequency of the N-H vibration rises (see strained small rings).

In aliphatic and aromatic amines, the intensity of the νNH_2 sym band is much higher than that of the νNH_2 asym band. This can be explained by the variation of the dipole moment of NH_2 bonds in which unshared electrons can be involved [33].



There is a linear relationship between the frequency of NH_2 vibrations in substituted aromatic amines and a number of thermodynamic and kinetic constants such as the kinetic Hammett- σ constant [35] (see also [16] and basicity [36-38]).

2. *Secondary amines* $R-NH-R$. In dilute solutions secondary amines have a single νNH band in the range $3300-3550\text{ cm}^{-1}$. In concentrated solution a second lower frequency band appears, arising from the hydrogen bonded form.

νNH frequencies in secondary aliphatic amines lie in the range $3310-3350\text{ cm}^{-1}$. The band is very weak [32]. In arylalkylamines $Ar-NH-R$ and diarylamines Ar_2NH , the frequency rises to $3430-3450\text{ cm}^{-1}$. Methylan-

line and ethylaniline absorb at 3430 cm^{-1} [30, 39] and diphenylamine, at 3433 cm^{-1} [40, 41]. The rise in frequency is followed by an increase in band intensity ($\epsilon=30-50$).

3. *Cyclic secondary amines.* Ethyleneimine absorbs at 3450 cm^{-1} in carbon tetrachloride solution [42, 43] and piperidine at 3347 cm^{-1} [43, 44]. In the solid state frequencies are lower. Pyrrolidine absorbs at 3125 cm^{-1} (KBr) [45] and ethyleneimine at 3341 cm^{-1} [46]. νNII frequency and band intensity in secondary amines belonging to a heterocyclic aromatic system depend on the nature of the heterocyclic ring and the polarity of the heteroatom.

b. **Hydrogen bonds in amines.** The νNH frequency is sensitive to change of state and decreases on going from the vapor to the liquid or solid state. The shift due to hydrogen bonding does not exceed 100 cm^{-1} , and in many instances it is of the same order of magnitude as shifts associated with change in solvent or change in state not involving hydrogen bonding. For this reason the interpretation of infrared spectra with respect to the formation of $\text{N}-\text{H}\cdots\text{N}$ bonds has been widely discussed.





One may assume that in nonpolar solvents (benzene, carbon tetrachloride, etc.) amines are free; for example, it is believed that in concentrated solutions of aniline or even in the pure liquid, no hydrogen bonding takes place [17]. In diphenylamine with a more acidic hydrogen atom, a shift of the νNII band by ca. 30 cm^{-1} is observed in the solid state cf. solution.

The low tendency of amines toward association is because of lower polarity of the $\text{N}-\text{H}$ bond. Increase in acidity of the hydrogen atom, like, for example, in diphenylamine and in five-membered ring heterocycles (pyrrole, imidazole, indole), leads to hydrogen bonding under appropriate conditions [48]. The $\text{N}-\text{H}$ group forms hydrogen bonds with alcohols. It has been shown that the shift in frequency is proportional to the pK_a of the amine [49, 55]. The tendency toward bond formation between the amine and the alcohol increases with the acidity of the OH group [51]. In aliphatic amines the capacity to act as electron donors toward CH_3OD can be seen from $\Delta\nu\text{OD}$ values shown in Table II-116. The νOD frequency (2689 cm^{-1}) in CH_3OD has been taken as standard [52].

Table II 116 Frequency shifts ($\Delta\nu\text{OD}$) in hydrogen bonding between amines and CH_3OD

| Bonded amine | νOD bonded | $\Delta\nu\text{OD}$ | pK_a |
|---------------------------|-----------------------|----------------------|--------|
| <i>n</i> -Butylamine | 2454 | 235 | 10.61 |
| <i>n</i> -Propylamine | 2439 | 250 | 10.59 |
| <i>Di-n</i> -butylamine | 2449 | 240 | 11.31 |
| <i>Di</i> ethylamine | 2421 | 268 | 10.98 |
| <i>Di</i> isopropylamine | 2131 | 258 | 11.05 |
| Tri- <i>n</i> -butylamine | 2446 | 243 | 9.93 |
| Triethylamine | 2400 | 289 | 10.78 |

The electron donating properties of cyclic amines vary with ring size. The following values are obtained on bonding with CH_3OD [38].

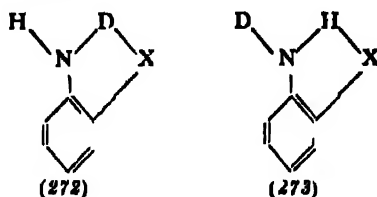
| | | | | |
|------------------------------|---|---|---|---|
| |  |  |  |  |
| $\nu\text{OD cm}^{-1}$ | 2468 | 2430 | 2427 | 2430 |
| $\Delta\nu\text{OD cm}^{-1}$ | 221 | 259 | 262 | 259 |
| pK_a (25°) | 8.04 | 11.29 | 11.27 | 11.22 |

The three-membered ring is the weakest proton donor and the weakest base toward the proton in water.

The binding of the NH bond to keto groups reduces the frequency to 3220–3240 cm^{-1} [53].

In a number of substituted aromatic amines, several bands occur in the νNH region. In some instances they were assigned to hydrogen bonded N–H linkages, for example, in β -naphthylamine, 2-aminoanthraquinone, *o*- and *m*-chloroaniline, *p*-phenylenediamine, *p*-nitroaniline, etc. [54, 55].

To prove the existence of conformational isomerism in ortho-substituted aromatic amines, partially deuterated amines RNHD have been used. *cis*- (272) and *trans*- (273) Isomers show two νNH bands and two νND bands characteristic for primary amines.



In compounds where $\text{X} = \text{CH}_3$, C_2H_5 , C_6H_5 , OCH_3 , and F , a single normal absorption was observed. In *o*-*tert*-butylaniline, the band is split (Table II-117) [56].

Table II-117 Characteristic frequencies in $\text{X-C}_6\text{H}_4\text{-NH}_2$, $\lambda\text{-C}_6\text{H}_4\text{-NHD}$, and $\text{X-C}_6\text{H}_4\text{-ND}_2$

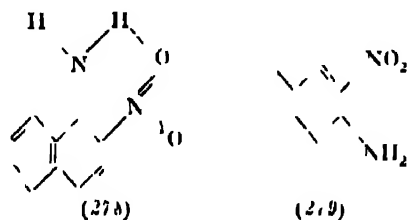
| Substituent λ | $\nu\text{N-H vibration}$ | | νNHD | $\nu\text{N-D vibration}$ | | νNDH |
|-------------------------------|---------------------------|------|-----------------|---------------------------|----------------------|-----------------|
| | νNH_2 | | | νND_2 | | |
| | asym | sym | | asym | sym | |
| 2- <i>tert</i> -Butyl | 3493 | 3402 | 3470 3425 | 2609 | 2492 | 2562 2531 |
| 2 <i>tert</i> -Butyl-5-chloro | 3503 | 3408 | 3476 3433 | 2616 | 2494 | 2571 2537 |
| 4 <i>tert</i> -Butyl | 3479 | 3394 | 3432 | 2597 | 2485 2455 2443 | 2534 |
| 2-Ethyl | 3480 | 3397 | 3436 | 2598 | 2485 2456 | 2538 |

Intramolecular hydrogen bonds. In molecules containing electron donating groups such as CO, COOR, NO₂, along with the amino group intramolecular hydrogen bonds are formed. These bonds are weak. Differences between associated and free bond frequencies are *small* and difficult to observe in NH absorptions, but can be detected more readily in the $\nu\text{C}=\text{O}$ or νNO_2 absorptions [54, 57, 58]. Frequency shifts in the following compounds are characteristic.

| | | | | |
|--------------------------------|-------|-------|-------|-------|
| | | | | |
| $\nu\text{CO}, \text{cm}^{-1}$ | 1730 | 1685 | 1730 | — |
| $\nu\text{NH}, \text{cm}^{-1}$ | — | 3361 | — | 3430 |
| | (274) | (275) | (276) | (277) |

N,N-Dimethylantranilic ester (274) shows the normal frequency of aromatic esters (1730 cm^{-1}). In *N*-methylantranilic ester (275), both νCO and νNH frequencies are lower. (For comparison, in carbon tetrachloride solution, νCO in methyl benzoate (276) is 1730 cm^{-1} and νNH in *N*-methylaniline (277), 3430 cm^{-1} .)

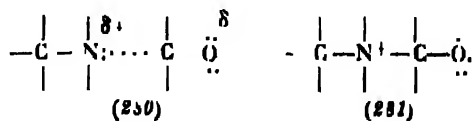
The intramolecular chelate hydrogen bond between adjacent NH₂ and NO₂ groups in nitronaphthylamine results in characteristic frequency shifts [58]. In dilute solutions of α -naphthylamine, the νNH asym band occurs at 3486 cm^{-1} , whereas in 1-nitro-2-aminonaphthalene it occurs at 3528 cm^{-1} . The NH sym absorption falls from 3412 cm^{-1} to 3378 cm^{-1} . Simultaneously, a change in νNO_2 frequency (1340 cm^{-1}) is observed. In this case chelation stabilizes structure (278).



In 2-nitro-3-aminonaphthalene (279), the weaker double bond character in the 2, 3-position is not sufficient to stabilize the chelate structure and the frequency remains unchanged (see also, „Diols”).

Large shifts are observed in chelate compounds of α , β -unsaturated β -amino-ketones [59].

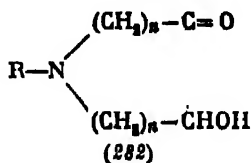
c. Transannular effects in aminoketones. The low νCO frequency in some ten-membered ring alkaloids is believed to be due to transannular effects (280) [60]



The complete disappearance of the carbonyl absorption has been explained by the formation of transannular bonds (281) [61]. Systematic studies of some 1-alkyl-1-azacyclanolones (aminoacyloines) (282) with rings containing 8–23 atoms ($R=CH_3, C_2H_5, C_6H_5$), have shown that transannular interactions depend on ring size and volume of the substituent R at the nitrogen atom [62–65]. The observed frequencies are shown in Table II–118.

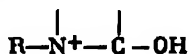
Table II–118 νCO and $\nu NH/OH$ frequencies (cm^{-1}) in azacyclanolones

| Compound | | | Free Base | | Perchlorate | |
|----------|---|----------------------|-----------|----------|-------------|-------------|
| R | n | Number of ring atoms | νCO | νOH | νCO | $\nu NH/OH$ |
| C_2H_5 | 2 | 7 | 1701 | 3458 | — | — |
| CH_3 | 3 | 9 | 1666 | 3410 | — | 3440 |
| C_6H_5 | 3 | 9 | 1671 | 3428 | — | 3425 |
| CH_3 | 4 | 11 | 1700 | 3462 | 1710 | 3480 |
| C_6H_5 | 4 | 11 | 1705 | 3470 | — | — |



1-Alkyl-1-azacyclanolones with 7-, 11-, 13-, 15-, 17-, 19-, 23-membered rings have normal absorptions at $1700\text{--}1710\text{ cm}^{-1}$. In 8-, 9-, and 10-membered rings, νCO frequencies are lower. The decrease is assigned to an interaction shown in (280). On perchlorate formation in the 9-membered ring compound the νCO absorption disappears completely because of the formation of a transannular bond (283).

The absorption reappears in the 11-membered ring [66].



(283)

The same effect occurs in more complicated systems. In compound (284), the νCO frequency decreases to 1664 cm^{-1} and in the corresponding perchlorate it disappears completely [67].


The effect of the volume of the substituent R at nitrogen on transannular interactions in eight- and nine-membered rings is interesting [62, 63].

In compound (285), increase in volume of the group R from methyl to *t*-butyl results in a rise in νCO frequency from 1666 to 1698 cm^{-1} . This means that the transannular interaction between the $C=O$ and $N-R$ groups is sterically hindered by the bulky substituent. The cyclopropane ring has a similar

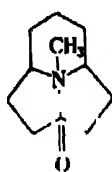
effect ($\nu CO=1695\text{ cm}^{-1}$). In the corresponding perchlorates $\text{R}-\text{N}^+-\text{C}-\text{OH}$

covalent bonds are formed only in compounds with $R=CH_3$, C_2H_5 , $(CH_3)_2CH$. In the perchlorate of (285), where $R=t$ -butyl, the νCO frequency is normal (1706 cm^{-1}). Frequency variation with substituents is shown in Table II-119.

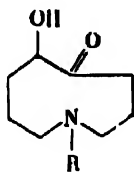
Table II-119 νCO and $\nu NH/OH$ frequencies (cm^{-1}) in 1-alkyl-1-azacyclanolones (285) and perchlorates

| R | Free Base | | Perchlorate | |
|---|-----------|-------------|-------------|-------------|
| | νCO | $\nu NH/OH$ | νCO | $\nu NH/OH$ |
| CH_3- | 1660 | 3410 | — | 3440 |
| C_2H_5- | 1671 | 3428 | — | 3425 |
| $(CH_3)_2CH-$ | 1691 | 3405 | — | 3435, 3285 |
| $(CH_3)_3C-$ | 1698 | 3480 | 1706 | 3331 |
|  | 1695 | — | — | — |

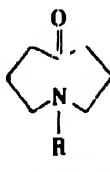
In the eight-membered ring aminoketone (286) with $R=CH_3$, the νCO frequency is 1683 cm^{-1} . In the perchlorate, the νCO absorption does not occur, and the νOH band arises at 3380 cm^{-1} (structure type 281). In compounds (285) and (286), where $R=\text{cyclopropyl}$ [e. g., (287)], the transannular effect is also diminished (νCO frequency = 1695 cm^{-1} , whereas for $R=\text{cyclohexyl}$ $\nu CO = 1687\text{ cm}^{-1}$).



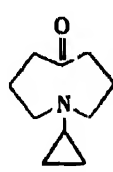
(284)



(285)



(286)



(287)

d. **N—H deformation vibrations.** In infrared spectra of primary amines, the NH deformation bands lie in the range $1560-1640\text{ cm}^{-1}$ (in plane deformation) and $650-900\text{ cm}^{-1}$ (out-of-plane deformation) [68].

Primary amines absorb between 1590 cm^{-1} and 1640 cm^{-1} . In aromatic amines, the band cannot be identified readily, being superimposed on bands arising from the aromatic ring. *o*-Chloroaniline absorbs at 1613 cm^{-1} , whereas *m*-chloroaniline has two bands in this region (1613 cm^{-1} and 1597 cm^{-1}).

The frequency of the deformation mode rises slightly on hydrogen bonding [69]. The out-of-plane deformation band occurs in all amines in the range $650-900\text{ cm}^{-1}$ and is generally broad [70].

In secondary aliphatic and cyclic amines, the δNH_2 absorption is very weak and difficult to identify. The probable region is $1490-1580\text{ cm}^{-1}$. In secondary aromatic amines, the absorption is superimposed on the ring vibration occurring in this region. On deuteration, a band at 1510 cm^{-1} was detected which could be assigned to a δNH vibration coupled with the νCN vibration [71].

e. **C—N stretching vibrations.** The frequency of the ν_{CN} vibration does not differ from that of C—C bonds, but the bands are stronger. In the aliphatic series, a medium intensity band occurring at $1028-1190\text{ cm}^{-1}$ is assigned to this vibration [18, 72].

Tertiary amines show two absorptions. Secondary amines have a band within the range $1095-1190\text{ cm}^{-1}$ [18, 72].

In aromatic amines frequencies are higher because of the increase in C—N bond order as a result of conjugation with the aromatic ring [18, 71].

Depending on the structure of the amine, the band occurs in the following regions:

| | cm^{-1} |
|-------------------|------------------------|
| primary amines, | 1250—1340; |
| secondary amines, | 1250—1350 (1241—1262); |
| tertiary amines, | 1310—1360. |

N-Alkylated aromatic amines show two bands, at $1250-1360\text{ cm}^{-1}$ and $1180-1280\text{ cm}^{-1}$. The higher frequency band was assigned to the $\text{C}_{\text{aryl}}-\text{N}$ bond and the lower frequency band to the $\text{C}_{\text{alkyl}}-\text{N}$ bond [69].

f. **The CH_3-N group.** The CH_3 group attached to a nitrogen atom in an aliphatic amine (CH_3-NHR) absorbs at $2780-2805\text{ cm}^{-1}$. Cyclic tertiary amines absorb in the same region. In aromatic N-methylamines (Aryl-NHCH_3), the frequency lies in the range $2815-2820\text{ cm}^{-1}$ [73].

The dimethylamino group $(\text{CH}_3)_2\text{N}$ is readily identifiable giving rise to two characteristic absorptions, at $2810-2825\text{ cm}^{-1}$ and $2765-2775\text{ cm}^{-1}$. Their extinction coefficients (ϵ) are 100–180 and 125–215, respectively. In addition, a weak absorption ($\epsilon=25-45$) occurs at 2730 cm^{-1} . If the dimethylamino group is attached to an aromatic ring, $\text{Aryl-N}(\text{CH}_3)_2$, a single absorption occurs at ca. 2800 cm^{-1} ($\epsilon=60-70$).

E. DERIVATIVES OF AMINES

a. Salts

With regard to vibration the $-\text{NH}_3^+$ group in salts of primary amines is analogous to the $-\text{CH}_3$ group, a broad, strong band at ca. 3020 cm^{-1} , the ammonium band, corresponds to symmetrical and asymmetrical $\nu_{\text{NH}_3^+}$ vibrations. This absorption overlaps with absorptions arising from the CH stretching mode. A medium intensity band sometimes occurs at 2500 cm^{-1} (assigned to an overtone).

The asymmetrical and symmetrical $\delta_{\text{NH}_3^+}$ vibrations are identified by absorptions at $1570-1600\text{ cm}^{-1}$ and 1500 cm^{-1} , respectively. They are difficult to distinguish, mainly in aromatic compounds.

Salts of secondary and tertiary amines have $>\text{NH}_3^+$ and $>\text{NH}^+$ groups and are characterized by a broad absorption in the range $2250-2700\text{ cm}^{-1}$. For

identification purposes the study of deformation modes in the 1600 cm^{-1} region is necessary.

Quaternary salts $R_4\overset{+}{N}$ do not have characteristic frequencies in the infrared.

b. Aminoxides

The vibration of the $N-O$ bond in aliphatic aminoxides $R_3N\rightarrow O$ gives rise to a very strong absorption at $950-970\text{ cm}^{-1}$ [74].

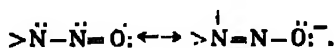
Heterocyclic tertiary amines absorb at much higher frequencies ($1200-1300\text{ cm}^{-1}$). Band positions in these structures depend on the electronic effect of the ring substituent (see Heterocyclic compounds [75]). The rise in frequency is attributed to the increase in $--N-\ddot{O}: \rightarrow$ bond order as a result of a larger contribution of the $N=O$ structure.

c. Nitroamines

The functional group of nitroamines consists of a nitro group attached to a nitrogen atom $-N-NO_2$. The asymmetrical νNO_2 stretching mode has approximately the same frequency as in nitro derivatives of hydrocarbons, $1530-1580\text{ cm}^{-1}$. The frequency of the symmetrical vibration lies in the range $1260-1290\text{ cm}^{-1}$ [76, 77].

d. Nitrosoamines

Vapors of monomeric alkylnitrosoamines $R_2N-N=O$ have a strong absorption at 1490 cm^{-1} . In carbon tetrachloride solution the absorption falls to 1450 cm^{-1} [78-81]. In the liquid state the dimeric form gives rise to an absorption at 1300 cm^{-1} , in the $\overset{+}{N}\rightarrow O^-$ vibration region of heterocyclic aminoxides, where the contribution of structures with $N=O$ double bonds is relatively large (see Dimers of nitroso-compounds):



F. AZOMETHINES

Azomethines $R-CH=N-R'$ (Schiff bases) have absorptions in the double bond region $1630-1690\text{ cm}^{-1}$ because of the $C=N$ group. Within these limits the $\nu C=N$ frequency in azomethines depends on the nature of the groups R and R' (see Table II-120) [82, 83].

The bands are of variable intensity. The intensity rises slightly on chain branching. In conjugated compounds the frequency falls and the bands become stronger.

In azomethines, where R and R' are alkyl or isoalkyl groups, the frequency lies in the range 1664–1672 cm^{-1} . Chain length or degree of branching does not have a marked influence on the vibration.

In phenylalkyl derivatives where the phenyl group is not conjugated with the C=N bond, the frequency falls slightly (1653–1669 cm^{-1}), regardless of whether the phenyl is R or R'.

Compared to compounds where R and R' = alkyl, compounds branched in the 2-position have a slightly higher frequency than those with normal chains or with branching in more remote positions.

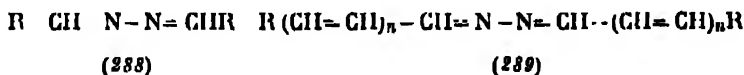
Conjugation with aromatic rings results in a decrease in $\nu\text{C}=\text{N}$ frequency to 1645–1650 cm^{-1} . Conjugation with C=C double bonds in unsaturated azomethines results in a slight decrease in frequency (1658–1664 cm^{-1}). The phenomenon is more intense in styryl derivatives.

Table II-120 $\nu\text{C}=\text{N}$ frequency in azomethines
R-CH=N-R'

| R | R' | $\nu\text{C}=\text{N}$, cm^{-1} |
|------------------------------------|-------------|---|
| Alkyl | Alkyl | 1664–1672 |
| Phenyl | Alkyl | 1629–1656 |
| Phenylalkyl | Phenylalkyl | 1653–1669 |
| Phenyl | Phenyl | 1645–1650 |
| Double bond (α , β) | Alkyl | 1658–1664 |

G. AZINES

Azines have a C=N double bond. Aldazines (288), similar to azomethines absorb at 1580–1670 cm^{-1} [84, 85]. Acetaldazine absorbs at 1664 cm^{-1} (CHCl_3). In spectra of azines of some polyenic aldehydes (289) with $n=2, 4, 6, 8$, and 10, several bands occur in the double bond region. In this case, the $\nu\text{C}=\text{N}$ vibration cannot be distinguished from $\nu\text{C}=\text{C}$. The highest frequency falls with increasing number of conjugated double bonds (see Alkenes). The main (stronger) bands have frequencies of 1600–1650 cm^{-1} and 1550–1580 cm^{-1} . Crotonaldehyde aldazine has three bands, at 1521, 1529, and 1650 cm^{-1} (in chloroform).



The CH deformation vibration in aliphatic azines gives rise to absorptions in the 1440–1450 cm^{-1} region.

In furfuralazine the frequency is higher (ca. 1470 cm^{-1}).

II. AZOXY COMPOUNDS $\text{R}-\text{N}=\text{N}-\text{R}$

$$\downarrow$$

$$\text{O}$$

The N→O group in aliphatic azoxy compounds gives rise to a band at 1250–1316 cm^{-1} and the N=N bond, at 1490–1515 cm^{-1} [86]. In the spec-

trum of azoxymethane $\text{CH}_3-\text{N}=\text{N}-\underset{\text{O}}{\underset{|}{\text{CH}}}_3$ the bands occur at 1342 and 1527 cm^{-1} and in $\text{F}_3\text{C}-\text{N}=\text{N}-\underset{\text{O}}{\underset{|}{\text{CF}}}_3$, at 1270 and 1579 cm^{-1} [87, 88]. The $\text{N}=\text{N}$ vibration in aromatic azoxy compounds could not be identified due to superimposition with aromatic bands and low intensity of the absorption.

I. AZOCOMPOUNDS $\text{R}-\text{N}=\text{N}-\text{R}$

The $\text{N}=\text{N}$ chromophore is characterized by its ultraviolet and visible spectrum. In the infrared, the absorption is weak even in asymmetrical molecules. In aromatic azocompounds aryl $-\text{N}=\text{N}-$ aryl bands have been observed at $1577 \pm 8 \text{ cm}^{-1}$ and $1046 \pm 14 \text{ cm}^{-1}$ [89, 90]. *trans*-Azobenzene absorbs at 1457, 970, and 750 cm^{-1} , and *cis*-azobenzene, at 1330 and 1225 cm^{-1} [91, 92]. The two isomers have a common band at 927 cm^{-1} which is absent in hydrazobenzene [91].

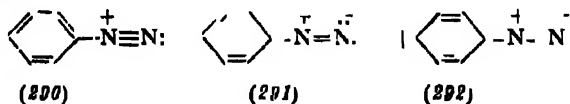
Some correlations based on molecular symmetry have been attempted for azobenzene and azobenzenes substituted in the 4,4' positions with halogen, methyl, ethyl, and methoxy groups in various solvents [93]. In polarized light all compounds clearly show dichroism in solid state [94].

J. DIAZOCOMPOUNDS

a. Diazonium salts

The characteristic absorption in diazonium salts is due to the cation $\text{Ar}-\text{N}_2^+$.

Electron distribution in diazonium salts is represented by structures (290), (291), and (292).



Structure (290) has the largest contribution. Consequently, the absorption of the CN_2 bond will occur in the triple bond region: 2237–2301 cm^{-1} ($\nu\text{C}\equiv\text{N}$, 2212–2257 cm^{-1} ; $\nu\text{N}\equiv\text{N}$, 2210–2300 cm^{-1}). Band position depends primarily on the structure of the cation. Changes in anions result in shifts of up to 40 cm^{-1} . The highest frequencies occur in fluoborates.

Frequencies of some benzenediazonium salts are shown in Table II-121 [95, 96].

Electron attracting substituents favoring structure (290) increase the νN_2 frequency; however, the effect is weak. Substituents with a strong +*E*-effect have considerable influence; for example, diazotized *p*-dialkylaminoanilines

absorb at 2137–2151 cm^{-1} . This is a proof for appreciable electron shifts toward structures (291) and (292).

In *p*-aminobenzene-diazonium fluoborate (2183 cm^{-1}), the contribution of structure (292) is smaller than in dialkyl-amino derivatives.

In diazosulfanilic acid (293), the frequency (2273 cm^{-1}) corresponds to a zwitterionic structure with triple bonded nitrogen.

Table II-121 νN_2 frequencies in diazonium salts [95, 59]

| Diazonium cation | Anion | νN_2 frequency, cm^{-1} |
|---|-------------------|---|
| $\text{C}_6\text{H}_5\text{N}_2^+$ | BF_4^- | 2283 |
| | ZnCl_2^- | 2268 |
| | FeCl_4^- | 2256 |
| | ICl_2 | 2257 |
| | Cl^- | 2252 |
| $p\text{-CH}_3\text{-C}_6\text{H}_4\text{N}_2^+$ | BF_4^- | 2283 |
| | ZnCl_2^- | 2257 |
| $p\text{-O}_2\text{N-C}_6\text{H}_4\text{N}_2^+$ | BF_4^- | 2306(2296) |
| $m\text{-HO-C}_6\text{H}_4\text{N}_2^+$ | BF_4^- | 2288 |
| $p\text{-(C}_6\text{H}_5)_2\text{N-C}_6\text{H}_4\text{N}_2^+$ | BF_4^- | 2151 |
| $p\text{-HO-C}_6\text{H}_4\text{N}_2^+$ | BF_4^- | 2110 |
| $\text{N}_2\text{C}_6\text{H}_4\text{-C}_6\text{H}_4\text{N}_2^+$ | BF_4^- | 2296 |
| | ZnCl_2^- | 2270 |

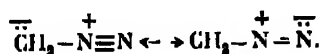
The large shifts in diazonium salts of *p*-aminophenol are due to the quinonediazide structure (see below).



(293)

b. Diazoalkanes, diazoalkenes

The first member of the series, diazomethane, has been extensively studied [97–100]. In its spectrum recorded in the gaseous phase, the N_2 vibration was assigned the 2100 cm^{-1} band. In solution this band occurs at 2075 cm^{-1} . The electronic structure of diazomethane is represented by structures (294) and (295) [101].

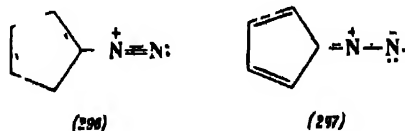


(294)

(295)

On substitution of hydrogen atoms in diazomethane with alkyl radicals, the frequency falls. In monosubstituted compounds R-CHN_2 the frequency is 2037–2019 cm^{-1} , and in disubstituted compounds R_2CN_2 , it is 2012–2033 cm^{-1} [102]. The frequencies are much lower than in aromatic diazo-compounds (ca. 2270 cm^{-1}). This shows a weaker triple bond character between the two nitrogen atoms and, consequently, a larger contribution of structure (295).

The predominance of structure (294) or (295) in substituted phenyldiazomethane depends on the nature of the substituent. Groups with a $-E$ effect (NO_2) shift the band toward higher frequencies and those with a $+E$ effect ($-\text{NR}_2$) shift the band toward lower frequencies. Diazocyclopentadiene (296) absorbs at 2083 cm^{-1} . Contribution of structure (297) is obvious [103].



Characteristic frequencies of some diazoalkanes, diazoketones, and diazoesters are shown in Table II-122.

Table II-122 Characteristic frequencies in diazo compounds, solution in carbon tetrachloride [104]

| Diazo compound | Frequency, cm^{-1} | | |
|---|-----------------------------|------------|------------|
| Diazoalkanes (R_1CN_2) | | | |
| CH_3N_2 | | 2075 | |
| CH_3CHN_2 | | 2037 | |
| $\text{C}_2\text{H}_5\text{CHN}_2$ | | 2045 | |
| $\text{C}_3\text{H}_7\text{CHN}_2$ | | 2041 | |
| $\text{C}_4\text{H}_9\text{CHN}_2$ | | 2037 | |
| $(\text{C}_6\text{H}_5)_2\text{CN}_2$ | | 2024 | |
| $p\text{-NO}_2\text{-C}_6\text{H}_4\text{CHN}_2$ | | 2044 | |
| $p\text{-(CH}_3)_2\text{N-C}_6\text{H}_4\text{CHN}_2$ | | 2012 | |
| Diazoketones (RCOCHN_2) | | | |
| $\text{C}_6\text{H}_5\text{COCHN}_2$ | 2092 | 1621 | 1360 |
| $p\text{-CH}_3\text{O-C}_6\text{H}_4\text{COCHN}_2$ | 2101 | 1621 | 1357 |
| $p\text{-NO}_2\text{-C}_6\text{H}_4\text{COCHN}_2$ | 2101 | 1629 | 1344 |
| $p\text{-CH}_3\text{-C}_6\text{H}_4\text{COCHN}_2$ | 2092 | 1647 | 1366, 1389 |
| $\alpha\text{-C}_{10}\text{H}_7\text{-COCHN}_2$ | 2088 | 1629, 1613 | 1348, 1335 |
| $\beta\text{-C}_{10}\text{H}_7\text{-COCHN}_2$ | 2092 | 1613 | 1366, 1339 |
| Diazoketones ($\text{RCO-CN}_2\text{-R'}$) | | | |
| $\text{C}_6\text{H}_5\text{COCN}_2\text{C}_6\text{H}_5$ | 2062 | 1623 | 1350 |
| $\text{C}_6\text{H}_5\text{COCN}_2\text{C}_2\text{H}_5$ | 2062 | 1613 | 1348 |
| Diazooesters (N_2CHCOOR) | | | |
| $\text{N}_2\text{CHCOOC}_2\text{H}_5$ | 2101 | 1695 | 1376, 1348 |

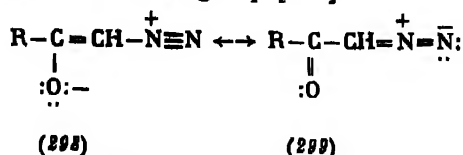
c. Diazoketones

Diazoketones are characterized by three strong bands, at $2058\text{--}2100\text{ cm}^{-1}$, $1600\text{--}1650\text{ cm}^{-1}$, and $1330\text{--}1390\text{ cm}^{-1}$. The first band occurs in ketones RCOCHN_2 at $2088\text{--}2101\text{ cm}^{-1}$, and in RCOCR'N_2 at $2058\text{--}2075\text{ cm}^{-1}$. (The majority of the latter compounds absorb, however, at $2058\text{--}2062\text{ cm}^{-1}$). The absorptions are assigned to the diazo group [104, 105].

The second band, assigned to the carbonyl vibration occurs between 1600 and 1650 cm^{-1} . In compounds with $\text{R}=\text{alkyl}$, it occurs constantly at $1645\text{--}1647\text{ cm}^{-1}$ (except diazocamphor and diazoacnaphthenone with strong bands at

1681–1685 cm^{-1}). When $R = \text{aryl}$ the frequency is slightly lower (1605–1629 cm^{-1}). All diazoketones have a third strong band at 1333–1389 cm^{-1} (sometimes doubled).

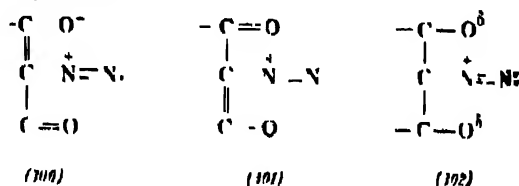
The higher νN_2 frequency in diazoketones is because of the contribution of structures such as (298), involving the carbonyl oxygen, which intensifies the triple bond character of the diazo group [104].



The rise in frequency of the diazo group parallels the decrease in $\nu\text{C}=\text{O}$ frequency.

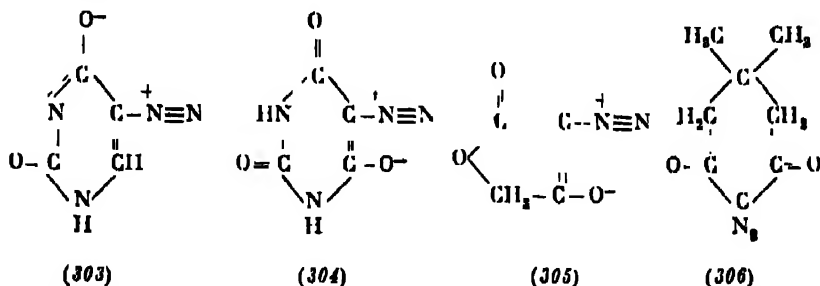
Shifts in the same direction also occur in *diazooesters*; for example, diazoacetic ester shows absorptions at 2101 (N_2), 1695 (CO), and 1348, 1376 cm^{-1} .

In diazoketones and diazoesters with several $\text{C}=\text{O}$ groups in the molecule, the contributions of betaine structures (300)–(302) can be evaluated from shifts of N_2 and $\text{C}=\text{O}$ frequencies.

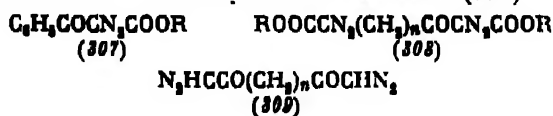


The effect of the CO group in diazoketones in favoring the betaine structure (300) is greater than that of the COOR group in diazoesters.

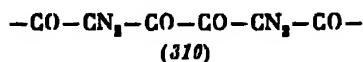
The highest frequency is observed in diazouracyl (303), diazobarbituric acid (304), and diazotetronic acid (305) (2151–2188 cm^{-1}), where the betaine structure (300) predominates.



In diazodimethyldihydroresorcinol (306) the contribution of structure (300) is lower (2151 cm^{-1} , along with two distinct absorptions at 2193 and 2257 cm^{-1}). The same situation occurs in benzoyldiazoacetic ester (307).

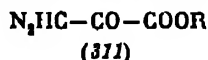


Contribution of structure (300) is less important also in bis-diazo- β -ketoesters (308) where $n=4, 5, \dots 7$ ($2146-2160\text{ cm}^{-1}$). bis-Diazoketones (309) ($n=4, 5, \dots 7$) with a single $\text{C}=\text{O}$ group next to the diazo group absorb at the lower end of the range. The frequency rises also in structures such as (310), corresponding to diazoesters (308) and diazoketones (309) where $n=0$. This is due to the increased contribution of structures (300), the same as in (303) and (304).



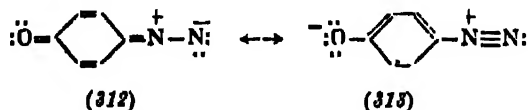
The rise in frequency of the diazo group parallels the fall in frequency of the $\text{C}=\text{O}$ group in the ketone or ester. The frequency of the carbonyl in diazoketones (309) is $1620-1626\text{ cm}^{-1}$. In benzoyldiazoacetic ester (307) the frequency falls to 1618 cm^{-1} under the influence of the benzene ring. In bis-diazoketoesters (308) the frequency rises with n ; for $n=1$, $\nu\text{CO}=1650\text{ cm}^{-1}$, $n=7$, $\nu\text{CO}=1667\text{ cm}^{-1}$.

Diazopyruvic ester (311) where the diazo group is not adjacent to the ester group has a normal absorption (same as in simple diazoketones), at 1626 cm^{-1} .



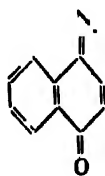
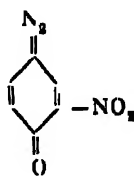
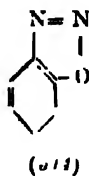
d. *Diazophenols, diazonaphthols (quinonediazides)*

The participation of structures (312) and (313) is obvious from frequencies



of the N_2 and $\text{C}=\text{O}$ groups. Diazophenols absorb at $2015-2173\text{ cm}^{-1}$ (diazo-group) and $1610-1640\text{ cm}^{-1}$ (νCO) [106, 107].

In *o*-quinonediazides cyclic structures such as (314) are excluded on the basis of infrared absorptions [106, 108].



$\nu\text{N}_2, \text{ cm}^{-1}$
 $\nu\text{CO}, \text{ cm}^{-1}$

2110
1618
(316)

2173
1618
(316)

2014
1618
(317)

| | | | |
|------------------------------|---------------|---------------|---------------|
| | | | |
| νN_2 , cm^{-1} | 2175, 2140 | 2175, 2130 | 2205, 2158 |
| νCO , cm^{-1} | 1620 (318) | 1613 (319) | 1613 (320) |

| | | |
|------------------------------|---------------|---------------|
| | | |
| νN_2 , cm^{-1} | 2017 | 2148 |
| νCO , cm^{-1} | 1622 (321) | 1610 (322) |

In a number of substituted quinonediazides (315)–(322) N_2 frequencies lie in the range 2091–2200 cm^{-1} . In many instances bands are split into two components of equal intensity. A weak band occurs at 2220 cm^{-1} [105–108].

The C=O group absorbs at 1620–1610 cm^{-1} (in the majority of cases, at 1620 cm^{-1}). This means that the C=O group is polarized, $>\overset{+}{C}=\overset{-}{O}$.

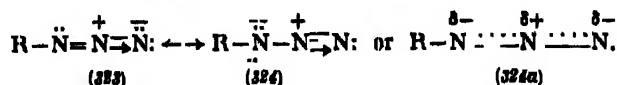
Frequency variation of the N_2 group in various diazo compounds is shown in Table II-123.

Table II-123 Frequency of the N_2 stretching vibration in diazo compounds [104]

| Compound | Frequency, cm^{-1} |
|---|-----------------------------|
| Aromatic diazonium salts (benzene, naphthalene) | 2232–2304 |
| Diazosulfanilic acid | 2268–2283 |
| Diazouracyl, diazobarbituric acid, diazotetronic acid | 2151–2188 |
| Diazodimethyldihydroresorcinol Benzoylethyl diazoacetate ester, Diazonium perbromides | 2212–2252 |
| β , β' -Dioxo- α , α' -bis-diazo-carboxylic ester | 2146–2180 |
| $ROOC-CN_2-CO-(CH_2)_n-CO-CN_2-COOH$ | |
| Diazotized <i>N</i> , <i>N</i> -dimethyl- <i>p</i> phenylenediamine | 2141–2151 |
| Azaserine | 2146 |
| Diazophenols, 2-diazonaphthols | 2110–2174 |
| bis-Diazo ketones, $N_2CHCO(CH_2)_nCOCHN_2$ | 2120–2128 |
| Diazoacetic ester | 2101 |
| Diazo ketones $RCOCHN_2$ | 2088–2101 |
| Diazocyclopentadiene | 2083 |
| Diazomethane | 2105; 2075 |
| Diazo ketones ($RCOCHN_2$, <i>R</i> and <i>R'</i> = alkyl, aryl) | 2058–2062 |
| Diazoalkanes, $R-CHN_2$ | 2037–2049 |
| Diazoalkanes, $R-CN_2-R'$ | 2012–2033 |
| 1-Diazonaphthol | 2016 |

K. AZIDES

The structure of the N_3 group is represented by structures (323) and (324).



The N_3 group has two vibration modes, symmetrical and asymmetrical. In inorganic azides with linear structure, the symmetrical vibration is inactive in the infrared; for example, crystalline ammonium azide absorbs at 2050 cm^{-1} (νN_3 , asym) and does not show any absorption in the symmetrical vibration region [109].

In organic azides the νN_3 asym frequencies lie in the range $2083-2140\text{ cm}^{-1}$. The absorptions arising from the symmetrical vibration are much more variable in position and lie in the range $1256-1351\text{ cm}^{-1}$ [110-113].

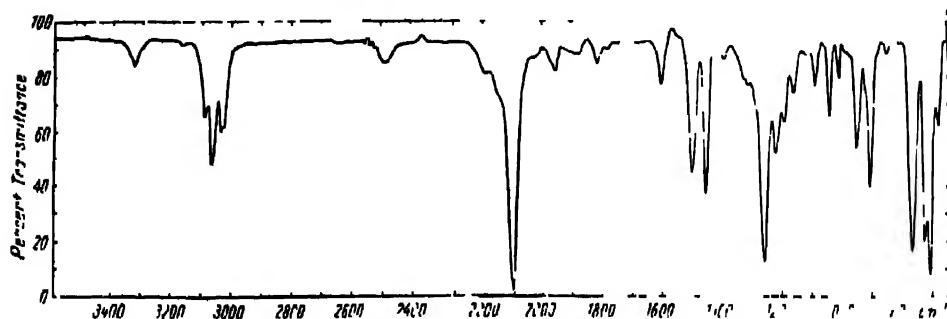


Fig. II-82 Infrared spectrum of triphenylmethyldiazide [113a].

Methyldiazide has a strong band at 2141 cm^{-1} and a weaker one at 1351 cm^{-1} [111]. In higher members, the frequency is slightly lower. *n*-Butyldiazide absorbs

Table II-124 νN_3 frequencies in aromatic azides RN_3 [112, 113a]

| R | νN_3 , asym | νN_3 , sym |
|------------------------|------------------|-----------------|
| Phenyl | 2144 | 1287 |
| Triphenylmethyl | 2103 | 1258 |
| <i>p</i> -Tolyl | 2092 | 1261 |
| <i>p</i> -Bromophenyl | 2110 | 1287 |
| <i>p</i> -Nitrophenyl | 2114 | 1285 |
| <i>m</i> -Chlorophenyl | 2096 | 1288 |
| <i>o</i> -Chlorophenyl | 2088 | 1297 |

at 2083 and 1256 cm^{-1} and *n*-decyldiazide, at 2092 and 1256 cm^{-1} . Cyclopentyldiazide and benzyl-diazide have the same absorption as *n*-butyldiazide (2083 and 1256 cm^{-1}) [112, 113]. Triphenylmethyldiazide absorbs at 2103 and 1258 cm^{-1} [113a] (Fig. II-82).

In aromatic azides the frequency varies with the position and nature of the substituent (Table II-124).

An increase in frequency is observed in the order phenyl, *p*-bromophenyl, and *p*-nitrophenyldiazide as a result of a greater contribution of the diazonium structure (324) (in diazonium salts the absorption occurs at 2260 cm^{-1}).


L. OXIMES

Aldoximes and ketoximes are characterized by absorptions of $O-H\cdots N-O$, and $C=N$ bonds in $C=N-OH$. The frequencies of these vibrations are [114–116]:

| Frequency | Free νOH | Bonded νOH | $\nu C=N$ | $\nu N-O$ |
|-----------|---------------|-----------------|------------------------|-----------|
| cm^{-1} | 3500–3650 | 3130–3300 | 1650–1685 1618–1660 | 990–960 |

a. νOH Stretching Vibration. In oximes of aliphatic carbonyl compounds, the free νOH vibration (gas or dilute solution) gives rise to absorptions at ca. 3600 cm^{-1} . The frequency falls by ca. 20 cm^{-1} on replacing the CH_3 groups in acetone oxime (3604 cm^{-1}) with two phenyl groups (benzophenone oxime, 3582 cm^{-1}). The decrease in frequency is larger in benzaldoxime (3501 cm^{-1}) than in acetaldoxime (3600 cm^{-1}). The decrease in frequency in the aromatic series is due to conjugation with the benzene ring. The νOH frequency in oximes is closer to that of phenols (phenol, 3605 cm^{-1}) rather than to that of alcohols ($C_6H_5CH_2OH$, 3622 cm^{-1}). The bonded OH band occurs at $3100\text{--}3300\text{ cm}^{-1}$. In most oximes (except benzaldoxime) it is doubled (see Table II-125).

Table II-125 Frequencies and extinction coefficients of νOH vibrations in oximes

| Oxime | Formula | Free νOH cm^{-1} | Bonded νOH cm^{-1} | ϵ_{max} Monomer ($cm^2/mole$) |
|---------------------|---|----------------------------|------------------------------|---|
| Acetaldoxime | $CH_3CH=NOH$ | 3600 | 3130 3300 | 168 |
| Acetone oxime | $(CH_3)_2C=NOH$ | 3604 | 3130 3290 | 157 |
| Benzophenone oxime | $(C_6H_5)_2C=NOH$ | 3582 | 3190 3290 | 226 |
| Benzaldoxime | $C_6H_5CH=NOH$ | 3501 | — 3315 | 261 |
| Cyclohexanone oxime |  NOH | 3600 | 3130 3280 | 186 |

The two bands can be interpreted as arising either from two different types of hydrogen bonds ($O-H\cdots O$ or $O-H\cdots N$), or they may arise from hydrogen bonds of polymeric or cyclic aggregates.

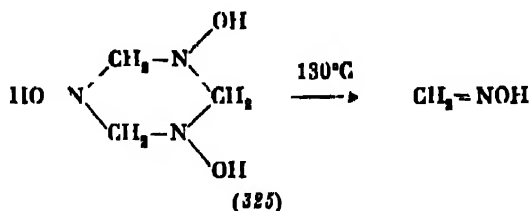
b $\nu C=N$ Vibration. Saturated, nonconjugated compounds have weak or medium absorptions at $1650\text{--}1685\text{ cm}^{-1}$. Acetone oxime absorbs at 1674 cm^{-1} (117); cyclopentanone oxime at 1681 , and cyclohexanone oxime at 1664 cm^{-1} (116). A rise in frequency in the five-membered-ring oxime is observed, which is in agreement with its increased strain (rise in frequency

in the five-membered ring, as compared to the six-membered ring, also takes place in other functional groups see Ketones, Anhydrides, etc.).

c. **N—O Vibration.** The N—O vibration has a strong absorption between 925 and 970 cm^{-1} (116). The frequency corresponds to a nitrogen-oxygen bond adjacent to a double bond.

Infrared spectra may provide some information concerning the geometrical isomerism of oximes (114).

1. **Formaldoxime.** At normal temperature formaldoxime $\text{CH}_2=\text{NOH}$ exists as a trimer with the probable structure (325). The spectrum of the monomer can be recorded only in vapor phase (117).



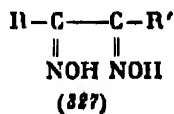
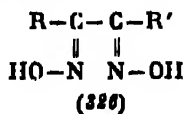
Frequency assignments for the first members of the series are shown in Table II-126.

Table II-126 (Characteristic frequencies in formaldoxime and acetone oxime in the vapor phase)

| Vibration | $\text{CH}_2=\text{NOH}$ | $(\text{CH}_3)_2\text{C}=\text{NOH}$ | $(\text{CH}_3)_2\text{C}=\text{NOD}$ |
|---------------------------|--------------------------|--------------------------------------|--------------------------------------|
| νOH monomer | 3646 | 3650 | 2688 |
| νCH_2 sym | 3098 | — | — |
| νCH_2 asym | 2976 | — | — |
| νCH_3 asym | — | 2924 | 2933 |
| νCH_3 sym | — | 2857 | 2874 |
| $\nu\text{C}=\text{N}$ | 1642 | 1662 | 1669 |
| δCH_2 sym | 1410 | — | — |
| δCH_2 asym | — | 1458 | 1451 |
| δCH_3 sym | — | 1377 | 1379 |
| δOH | 1315 | 1340 | 985 |
| δCH_2 asym | 1154 | 1086 | — |
| γCH_2 | — | 1051 | 1055 |
| $\omega\text{N}-\text{O}$ | 888 | 922 | 917 |

The spectrum of acetone oxime in the crystalline state or in solution shows large shifts in νOH frequencies (3185 cm^{-1}), δOH frequencies (1177 cm^{-1}), and $\nu\text{C}=\text{N}$ frequencies (1672 cm^{-1}).

2. **Dioximes.** Spectra of dioximes (glyoximes) show some special features connected with the configuration of the molecule. Frequency shifts are of value in distinguishing *anti* (326) and *amphi* (327) isomers



Frequency assignments based on studies of aliphatic, alicyclic, and halo dioxime spectra [118-121] are shown below:

| Frequency | νOH | $\nu\text{C}=\text{N}$ | $\nu\text{N}=\text{O}$ | δOH | νOH |
|------------------|----------------|------------------------|------------------------|-------------------|----------------|
| cm^{-1} | 3175 3336 | 1610-1640 | 950-1000 | 1450-1530 | 760 |

Comparison of methyl- and dimethylglyoxime with monochloro- and dichloroglyoxime and the corresponding deuterated compounds [118] shows that the halogen atom reduces the $\nu\text{N}=\text{O}$ frequency and doubles the $\text{C}=\text{N}$ band (Table II-127).

Table II-127 Characteristic frequencies in dioximes (in KBr) [118]

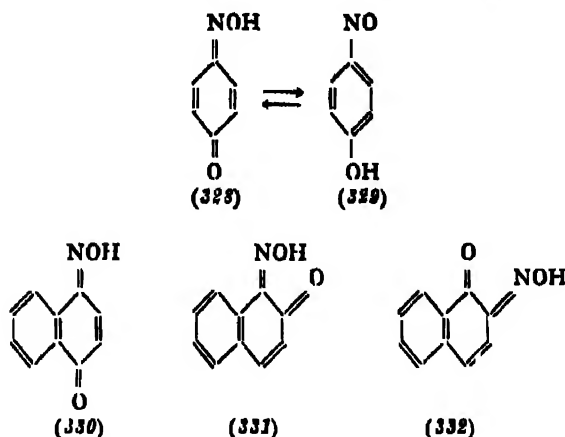
| Compound | νOH (cm^{-1}) | | $\nu\text{C}=\text{N}$ | $\nu\text{N}=\text{O}$ | δOH |
|------------------------------|-------------------------------------|------------|------------------------|------------------------|-------------------|
| | Dioxane solution | in KBr | | | |
| Methylglyoxime | 3289 | 3195, 3247 | 1621 w | 952 | 1433 |
| Dimethylglyoxime | 3300 | 3215 | 1621 w | 979 | 1441 |
| Dichloroglyoxime | 3236 | 3257 | 1623 w | 1000 | 1410 |
| <i>amphi</i> -Chloroglyoxime | 3247 | 3155, 3236 | 1626, 1592 | 968 | 1271 |
| <i>anti</i> -Chloroglyoxime | 3268 | 3155, 3289 | 1610 w | 978 | 1403 |

The $\nu\text{C}=\text{N}$ vibration in *anti*-glyoximes gives rise to a weak absorption at 1621 cm^{-1} , corresponding to a centrosymmetrical structure (326). *amphi*-Chloroglyoxime has a doublet of medium intensity assigned to the *s-cis* configuration (327).

νOH vibration. In concentrated solutions or in KBr, glyoximes absorb at 3125-3300 cm^{-1} (bonded νOH). The frequency of the bonded hydroxyl is higher in chloro compounds. In *amphi*-chloroglyoxime the absorptions due to the bonded hydroxyl (3155 and 3236 cm^{-1}) disappear on dilution; however, a band at 3217 cm^{-1} persists. It is assigned to the intramolecularly bonded hydroxyl. On dilution the other compounds show a single band at ca. 3300 cm^{-1} .

The $\text{N}=\text{O}$ frequency does not change much with configuration. However, it changes with the nature of substituents rising from 952 cm^{-1} in dimethylglyoxime to 978 cm^{-1} in *anti*-chloroglyoxime and 1000 cm^{-1} in the dichloro derivative (118).

3. *Quinone oximes*. Spectra of quinone oximes are much more complicated than those of simple oximes due to the tautomerism (328) \rightleftharpoons (329).



In the solid state or in nonpolar solvents, the quinone oxime form (328) predominates. Nitrosonaphthols- 1,4 and- 1,2 show the same tautomerism. The characteristic frequencies are shown in Table II-28.

Table II-28 Characteristic frequencies in quinone monooximes [122]

| Compound | $\nu\text{C}=\text{O}$ | | Deuterated | $\nu\text{C}=\text{N}$ | δOH | $\nu\text{N}-\text{OX}$ $\text{X}=\text{H}$ $\text{X}=\text{CH}_3$ |
|----------------------------------|------------------------|-------------------|------------|------------------------|-------------------|--|
| | Solid | In CCl_4 | | | | |
| 1,4-Benzoquinone oxime (328) | 1628 | 1648 | 1632 | 1555 | 1450 | 1037 |
| 1,4-Naphthoquinone oxime (330) | 1630 | 1655 | 1626 | 1577 | 1442 | 975 |
| 1,2-Naphthoquinone-2-oxime (332) | 1668 | 1680 | 1669 | 1550 | 1432 | 1069 |
| 1,2-Naphthoquinone-1-oxime (331) | 1618 | 1632 | 1616 | 1526 | — | 1076 |

The data show that the $\nu\text{C}=\text{O}$ frequency is close to that of 1,4-benzoquinone (1667 cm^{-1}) or 1,2- and 1,4-naphthoquinone (1678 , 1675 cm^{-1} , respectively). It also corresponds to the νCO frequency in oxime ethers. The low frequency in 1,2-naphthoquinone-1-oxime is due to chelation.

The $\nu\text{C}=\text{N}$ frequency is much lower than in nonconjugated oximes. The band is strong, cf. aromatic aldoximes and ketoximes which give rise to weak absorptions.

The increased $\nu\text{N}-\text{O}$ frequency (1075 cm^{-1}), cf. simple oximes ($930\text{--}960\text{ cm}^{-1}$), is believed to be due to a larger participation of a nitroso structure, where the $\text{N}-\text{O}$ bond order is increased [122].

M. ESTERS OF NITRIC ACID (NITRATES RONO_2)

Nitrates contain the bond $\text{O}-\text{NO}_2$. Their infrared spectra show absorptions arising from NO_2 stretching and deformation vibrations and from the $\text{O}-\text{N}$ vibration.

Frequency assignments, by analogy with nitric acid are shown in Table II-129 [2, 5, 123-125].

In secondary alkyl nitrates the 1282 cm^{-1} band is often split into a doublet.

Straight-chain alkyl nitrates show a band at 724 cm^{-1} . Its intensity increases with chain length. The band arises from the γCH_2 vibration. The ratio between the intensity of this band and that of the 757 cm^{-1} band (γNO_2) may be a measure of chain length.

Methyl nitrate has two strong bands, 1629 cm^{-1} and 1276 cm^{-1} and a broad central band at $851-870\text{ cm}^{-1}$ [1, 126].

Primary and secondary alkyl nitrates belonging to the alkane series with 2-16 carbon atoms have strong absorptions shown in Table II-129 [4, 125].

In cyclopentyl and methylcyclohexyl nitrates, νNO_2 bands occur at 1630 and 1277 cm^{-1} and $\nu\text{O}-\text{N}$ bands, at 860 cm^{-1} . 2-Phenylethyl nitrate has the same absorptions.

Table II-129 Characteristic frequencies in nitrates

| Vibration | Frequency, cm^{-1} |
|------------------------|-----------------------------|
| νNO_2 asym | 1620-1640 |
| νNO_2 sym | 1272-1282 |
| $\nu\text{O}-\text{N}$ | 855-870 |
| γNO_2 | 756-760 |
| δNO_2 | 694-708 |

N. ESTERS OF NITROUS ACID (NITRITES, $\text{RO}-\text{N}=\text{O}$)

Spectra of alkyl nitrites show a doublet at $1650-1680\text{ cm}^{-1}$ and $1613-1625\text{ cm}^{-1}$ [127-131] that was assigned to the NO stretching vibrations. The relative intensity of the two absorptions varies with temperature; therefore, the existence of an equilibrium mixture of *syn* and *anti* isomers was assumed (127). The higher frequency arises from the *anti* isomer and the lower frequency from the *syn* isomer (Table II-130) [127, 129, 132].

Table II-130 Characteristic frequencies in nitrites

| Nitrites (vapor) | <i>syn</i> form | | | <i>anti</i> form | | |
|---|---------------------|---------------------|------------------------------|---------------------|---------------------|------------------------------|
| | $\text{N}=\text{O}$ | $\text{O}-\text{N}$ | $\text{O}-\text{N}=\text{O}$ | $\text{N}=\text{O}$ | $\text{O}-\text{N}$ | $\text{O}-\text{N}=\text{O}$ |
| $\text{CH}_3\text{O}-\text{N}=\text{O}$ | 1625 | 811 | 617 | 1681 | 814 | 565 |
| $\text{RC}_2\text{H}_5-\text{O}-\text{N}=\text{O}$ | 1620 ± 2 | 820 ± 10 | 680 ± 2 | 1674 ± 4 | 795 ± 5 | 600 ± 20 |
| $\text{R}_1\text{R}_2\text{CH}-\text{O}-\text{N}=\text{O}$ | 1615 ± 2 | — | 680 ± 2 | 1665 ± 1 | 779 ± 4 | 599 ± 6 |
| $\text{R}_1\text{R}_2\text{R}_3\text{C}-\text{O}-\text{N}=\text{O}$ | 1612 ± 2 | — | 680 | 1653 ± 1 | 758 ± 7 | 617 ± 4 |

The frequency depends on the nature of the alkyl group. It decreases in the order methyl > primary alkyl > secondary alkyl > tertiary alkyl.

The equilibrium shifts toward the *anti* form with increasing size of the alkyl group.

The temperature dependence of the equilibrium between the two isomers and the fact that bulky substituents favor the *anti* form suggest the existence of a conformational isomerism made possible through free rotation about the N—O bond.

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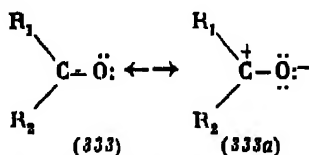
CHAPTER 6

CARBONYL COMPOUNDS

The presence of a carbonyl group in organic compounds gives rise to a strong absorption between 1650 and 2000 cm^{-1} . This absorption is one of the most extensively studied with regard to both frequency and band intensity. It is the most representative type of vibration localized in an individual bond.

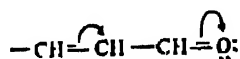
The frequency of vibration arising from the carbonyl group depends primarily on the force constant. The mass of atoms or atomic groups attached to the carbon atom affects the frequency to a much lesser extent.

The factors determining vibrations in the force constant are electronic effects (inductive and conjugative), electric field effects, and steric effects. These effects are cumulative and the contribution of any one of them can be estimated only approximately. Under the influence of these factors, the electronic distribution in the carbonyl group is best represented either by structure (333) or (333a).



The R_1 and R_2 groups can exert an inductive effect $+I$ or $-I$. If they are electron donating ($+I$) (alkyl, cycloalkyl), electronic shifts toward structure (333a) are favored. The bond order falls; the force constant is lowered. Hence the frequency decreases.

For example, in the series formaldehyde, acetaldehyde, acetone, on substitution of the hydrogen atoms with one or two methyl groups, respectively, the νCO frequency falls from 1750 cm^{-1} (formaldehyde) to 1745 cm^{-1} (acetaldehyde) and 1718 cm^{-1} (acetone). In the case of electron withdrawing groups ($-I$) (alkenyl, alkynyl, and aryl) the $-I$ effect is dominated by the conjugative effect and instead of rising, the frequency of the carbonyl group falls; for example, acrolein absorbs at 1723 cm^{-1} cf. acetaldehyde which absorbs at 1745 cm^{-1} .



(334)

Substitution of the R_1 and/or R_2 group in formula (333) with Hal , OH , OR , NH_2 , NR_2 , etc. with opposite I and E effects leads to different classes (acid chlorides, acids, and functional derivatives of the carboxyl group). They are described in the following chapters. Characteristic vibrations of complexes with metal carbonyls show a special behavior.

The electric field effect can occur in molecules in which the carbonyl group is situated at a convenient distance from another polar group. Such a situation is encountered in some conformational isomers of α -halocarbonyl compounds.

The steric effect results in a certain configuration of the molecules, inhibition of conjugation, or, in the case of cyclic compounds, in ring strain.

The position of absorption bands arising from the carbonyl group can also be affected by intra- and intermolecular hydrogen bonding, physical state, and solvent [1].

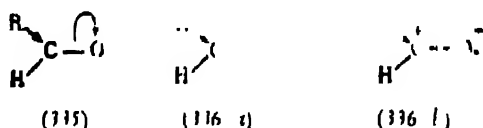
The highly polar character of the carbonyl group gives rise to strong absorptions in the infrared. The fact that the band does not overlap with other bands is of special analytical value. As opposed to the Raman spectrum, in the in-

frared spectrum the integrated absorption does not vary much with the carbonyl type. In this region it can be used only to determine the number of carbonyl groups in the molecule [1]. Larger variations in intensity are found in α,β -unsaturated carbonyl compounds.

The C=O group has an influence on vibrations of adjacent bonds giving rise to characteristic absorptions of C-H and C-C bonds. Mutual influences between the carbonyl and other functional groups will be discussed in subsequent sections.

ALDEHYDES

The carbonyl group in aldehydes is attached to a hydrogen atom and an organic group R (335)



The group -C(H)=O can be identified in the infrared both by the C=O stretching vibration and the characteristic C-H vibration

In the first member of the aliphatic series, formaldehyde, the carbonyl group is attached to two hydrogen atoms. The six normal vibration modes of the planar molecule (CH_2O (C_{2v} symmetry)) are all active both in Raman and the infrared [2] (Table II-131)

Table II-131 Fundamental frequencies in $\text{H}_2\text{C}=\text{O}$ and $\text{D}_2\text{C}=\text{O}$ (gas) [2]

| ν vacuum, cm^{-1} | | Assignment and band type | Species | Vibration |
|--------------------------------|-------------------------------|---|---------|-------------------------------|
| $\text{H}_2\text{C}=\text{O}$ | $\text{D}_2\text{C}=\text{O}$ | | | |
| 1167 s | s ^a | ν_{H} s | B_1 | $\delta(\text{H})$ |
| 1260 | 997 | $\nu_{\text{C}} \parallel$ | A_1 | $\delta(\text{H})$ |
| 1503 | 1105.7 | ν_{H} s | A_1 | $\delta(\text{H})$ |
| 1713.6* | 1700 | $\nu_{\text{C}} \parallel \nu_{\text{O}}$ | A_1 | $\nu(\text{C}=\text{O})$ |
| 2780 | 2055.8 | $\nu_{\text{H}} \parallel \nu_{\text{O}}$ | A_1 | $\nu(\text{C}-\text{H})$ sym |
| 2874 | 2159.7 | ν_{H} s | B_1 | $\nu(\text{C}-\text{H})$ asym |

* According to other sources 1710 cm^{-1} [2] or 1716 cm^{-1} [3]. The strong band occurring in the spectrum of formaldehyde at 2973 cm^{-1} and in deuterioformaldehyde at 2208 cm^{-1} corresponds to the $2\nu_{\text{H}}$ overtone coupled by 1 cm resonance with the ν_{H} vibration

In spectra of higher members the position and intensity of the C=O band are influenced by the hydrocarbon radical R

The influence of the C=O group on adjacent bonds results in shifts of the C-H vibration in -C(H)=O toward lower frequencies.

1. Saturated Aliphatic Aldehydes

a. $\nu\text{C}=\text{O}$ Vibration. Substitution of a hydrogen atom in formaldehyde by an alkyl group results in a decrease of the $\text{C}=\text{O}$ frequency. In the vapor phase acetaldehyde absorbs at 1745 cm^{-1} . In carbon tetrachloride solution, the frequency falls to 1730 cm^{-1} and in acetonitrile (polar solvent) to 1723 cm^{-1} [4, 5]. In carbon tetrachloride solution, bands of the higher members of the series lie in the range $1720\text{--}1740\text{ cm}^{-1}$ [6]. Lengthening of the alkyl chain does not alter the frequency of the carbonyl group; for example, propionic aldehyde has the same $\nu\text{C}=\text{O}$ frequency (1736 cm^{-1}) as heptanal [4]. This shows that the mass effect associated with increase in chain length is negligible. The slight decrease in frequency on substitution of the hydrogen atom in $\text{CH}_2=\text{O}$ with an alkyl group is mostly due to the electron-donating $+I$ effect of the alkyl group, favoring structure (336b).

A smaller effect was observed with higher alkyl groups cf. the methyl group. This results in a slight increase in frequency in higher members of the series (ca. 5 cm^{-1}).

b. $\text{C}-\text{H}$ Vibration. The frequency of the $\text{C}-\text{H}$ stretching vibration in the aldehyde group differs from that of CH_3 , CH_2 , and CH groups in hydrocarbons. The theory predicts a decrease in frequency to $2700\text{--}2900\text{ cm}^{-1}$ [7]. Many aldehydes show two bands in this region, at 2720 cm^{-1} and 2820 cm^{-1} [8]. No definite assignments for these bands exist at the present time. One of them is considered to be a combination band or an overtone. At any rate, the presence of an absorption at 2720 cm^{-1} along with the position of the $\nu\text{C}=\text{O}$ band are spectroscopic proofs for the existence of an aldehyde group in the molecule [9, 10]. The two absorptions also occur in unsaturated aldehydes (Fig. II-83).

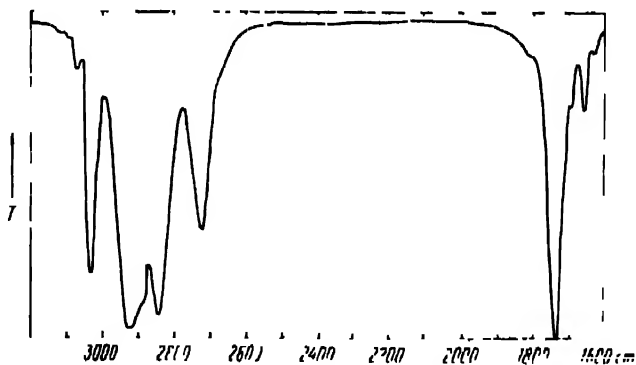
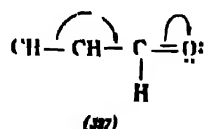


Fig. II-83 Infrared spectrum of 3-cyclohexenylacetaldehyde.

2. Unsaturated Aldehydes

a. α,β -Unsaturated aldehydes with one double bond. The presence of an isolated double bond remote from the carbonyl group does not alter the $\nu\text{C}=\text{O}$ frequency.

In α,β -unsaturated aldehydes, the favored structure is (337) in which both the $C=C$ and $C=O$ bond orders are reduced. The weak $-I$ effect of the $C=C$ double bond is overshadowed by the conjugative effect which in this case acts in the same direction as the $-I$ effect of the CHO group. The force constant is lowered. Hence, the frequency of the two bonds falls [11].



1. νCO *Stretching vibration*. In α,β -unsaturated aldehydes, the carbonyl frequency lies in the range $1685-1705 \text{ cm}^{-1}$. The mean value is 1695 cm^{-1} [6]. Within these limits, the frequency is higher in compounds with a terminal double bond. $\nu C=C$ and $\nu C=O$ frequencies and band intensities of some α, β -unsaturated aldehydes are shown in Table II-132.

Table II-132 $\nu C=O$ and $\nu C=C$ frequencies in α,β -unsaturated aldehydes [12]

| Aldehyde | $\nu C=O$ cm^{-1} | $\int \epsilon d\lambda$ cm^2/mole | $\Delta\nu/2$ cm^{-1} | $\nu C=C$ cm^{-1} | $\int \epsilon d\lambda$ | $\Delta\nu/2$ |
|---|-------------------------------|---|-----------------------------------|-------------------------------|--------------------------|---------------|
| $\text{CH}_2=\text{CH}-\text{CH}=\text{O}$ | 1703 | 7.25 | 7.0 | 1620 | 0.19 | 19.0 |
| $\text{CH}_3-\text{C}(\text{H})=\text{CH}-\text{CH}=\text{O}$ | 1702 | 5.70 | 5.0 | 1638 | 0.6 | — |
| $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{O}$ | 1700 | 8.40 | 5.5 | 1644 | 1.37 | 7.0 |
| $\text{CH}_3\text{CH}_2-\text{CH}=\text{C}(\text{H})-\text{CH}=\text{O}$ | 1693 | 7.90 | 7.0 | 1645 | 1.76 | 16.0 |
| $\text{CH}_3-\text{C}(\text{H})_2-\text{CH}=\text{CH}-\text{CH}=\text{O}$ | 1686 | 7.60 | 6.0 | 1638 1621 | 1.43 | 10.5 10.0 |

Acrolein absorbs at 1723 cm^{-1} in the vapor phase [4] and at 1703 cm^{-1} in tetrachloroethylene [12]. An alkyl group at the $C=C$ double bond slightly lowers the frequency; for example, β -methylcrotonic aldehyde absorbs at 1686 cm^{-1} .

The mean value of the νCO band intensity, $7.8 \text{ cm}^2/\text{mole}$, is higher than in saturated ketones (mean value $5.1 \text{ cm}^2/\text{mole}$) [12].

2. $\nu C=C$ *Stretching Vibration*. In α,β -unsaturated aldehydes with a terminal double bond (see Table II-132), the $\nu C=C$ frequency falls, having a mean value of 1625 cm^{-1} . The bands are relatively weak (mean value $0.75 \text{ cm}^2/\text{mole}$) cf. aldehydes with an internal conjugated double bond ($2.0 \text{ cm}^2/\text{mole}$).




On comparing the characteristics of $\nu C=O$ and $\nu C=C$ bands, it has been observed that whereas the intensity of the $\nu C=O$ absorption varies by no

more than a factor of 2, the $\nu\text{C}=\text{C}$ band intensity varies within much larger limits. This is because of the possibility of much larger dipole moment variations in the nonpolar $\text{C}=\text{C}$ bond than in the highly polar $\text{C}=\text{O}$ bond [12].

b. Conjugated polyenic aldehydes.

1. $\nu\text{C}=\text{O}$ stretching vibration. In α, β -unsaturated aldehydes with two conjugated double bonds, the presence of the second double bond results in a decrease in frequency of $\nu\text{C}=\text{O}$ of ca. 10 cm^{-1} . For instance, crotonic aldehyde absorbs at 1685 cm^{-1} in chloroform solution and at 1715 cm^{-1} in the vapor phase. Under the same conditions, 2,4-hexadienal absorbs at 1677 and 1705 cm^{-1} , respectively [13]. A number of polyenic aldehydes $\text{CH}_2(\text{CH}=\text{CH})_n\text{CHO}$ where $n=2 \dots 7$ (Table II-133) absorb in the range $1664\text{--}1677\text{ cm}^{-1}$.

Table II-133 Characteristic frequencies in polyenic aldehydes

| Aldehyde | $\nu\text{C}=\text{O}\text{ cm}^{-1}$ | | $\nu\text{C}=\text{C cm}^{-1}$ | |
|--|---------------------------------------|-----------------------------|--------------------------------|-----------------------------|
| | Vapor | Solution in CHCl_3 | Vapor | Solution in CHCl_3 |
| $\text{CH}_3\text{--CH=CH--CHO}$ | 1715 | 1685 | 1650 | 1638 |
| $\text{CH}_3\text{--(CH=CH)}_2\text{--CHO}$ | 1705 | 1677 | 1650 | 1642 |
| $\text{CH}_3\text{--(CH=CH)}_3\text{--CHO}$ | | 1674 | | 1615 |
| $\text{CH}_3\text{--(CH=CH)}_4\text{--CHO}$ | | 1673 | | 1592 |
| $\text{CH}_3\text{--(CH=CH)}_5\text{--CHO}$ | | 1664 | | 1570 |
| | | | | 1615 |
| $\text{CH}_3\text{--(CH=CH)}_6\text{--CHO}$ | | 1671 | | 1561 |
| | | | | 1615 |
| $\text{CH}_3\text{--(CH=CH)}_7\text{--CHO}$ | | 1674* | | 1546 |
| | | | | 1611 |
|  CH=CH--CHO | | 1677 | | 1628 |
|  $(\text{CH=CH})_2\text{--CHO}$ | | 1677 | | 1615 |
| | | | | 1608 |
|  $(\text{CH=CH})_3\text{--CHO}$ | | 1671 | | 1558 |
| | | 1668* | | 1608 |
| | | | | 1549* |
| | | | | 1614* |

* Liquid film.

This shows that lengthening of the polyenic chain does not influence the frequency of the carbonyl group. The same effect was observed in α -furyl-aldehydes [13] with long polyenic chains (Table II-133). 3-furylacrolein absorbs at 1677 cm^{-1} (in chloroform). In compounds containing up to six conjugated double bonds between the CHO group and the furan ring, the νCO frequency is $1668\text{--}1677\text{ cm}^{-1}$. (A decrease in frequency of ca. 10 cm^{-1}

is observed in spectra recorded in liquid films). In octatriene dialdehyde (338), the ν_{CO} frequency is 1680 cm^{-1} [11].



(338)

2. $\nu_{\text{C}=\text{C}}$ *Stretching vibration*. In addition to the $\nu_{\text{C}=\text{O}}$ band of relatively constant frequency, polyenic aliphatic aldehydes show a band in the 1600 cm^{-1} region assigned to the $\text{C}=\text{C}$ double bond vibration. Its frequency decreases with increasing the number of double bonds in the molecule. However, the double bond increment decreases with chain lengthening so that in long chains the $\nu_{\text{C}=\text{C}}$ frequencies are approximately equal.

Crotonic aldehyde absorbs in the vapor phase at 1650 cm^{-1} and in solution (CHCl_3) at 1638 cm^{-1} . In polyenic aldehydes $\text{R}(\text{CH}=\text{CH})_n\text{CHO}$ with $n=2, 3, \dots, 7$, the $\nu_{\text{C}=\text{C}}$ frequency gradually falls from 1638 to 1561 cm^{-1} . In liquid films the frequency is slightly lower [13].

c. α, β -unsaturated aldehydes with a triple bond. When the carbonyl group is conjugated with a triple bond between the α - and β -carbons, the $\nu_{\text{C}=\text{O}}$ frequency decreases by about the same amount as in aromatic aldehydes. Propargyl aldehyde $\text{HC}\equiv\text{C}-\text{CHO}$ absorbs at 1692 cm^{-1} . On deuteration of the aldehyde CH bond, the frequency falls by 20 cm^{-1} because of the mass effect of deuterium. The characteristic frequencies of propargyl aldehyde and some deuterated derivatives are shown in Table II-134.

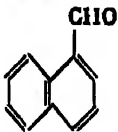
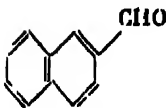
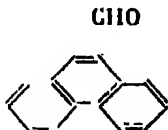
Table II-134 Characteristic frequencies (cm^{-1}) in propargyl aldehyde

| HC C-CHO | HC C ² DO | DC CCHO | Assignments |
|----------|----------------------|---------|-----------------------------------|
| 3335 | 3300 | 2620 | $\nu_{\text{C}-\text{H}}$ |
| 2869 | | 2880 | $\nu_{\text{C}-\text{H}}$ ald. |
| - | 2130 | - | $\nu_{\text{C}-\text{D}}$ ald. |
| 2125 | 2110 | 1990 | $\nu_{\text{C}\equiv\text{C}}$ |
| 1692 | 1670 | 1682 | $\nu_{\text{C}=\text{O}}$ |
| 1398 | 1076 | 1379 | deform. HCO |
| 950 | 871 | 923 | $\nu_{\text{C}-\text{C}}$ |
| 691 | 681 | 542 | deform. $\text{CH}\equiv\text{C}$ |

3. Aromatic Aldehydes

$\nu_{\text{C}=\text{O}}$ frequencies in aromatic aldehydes Aryl-CHO are lower than in acetaldehyde due to conjugation of the carbonyl group with the aromatic ring. The mean value in the liquid phase is 1705 cm^{-1} and on the vapor phase,

1722 cm^{-1} [4]. Frequencies of some representative compounds (in CCl_4) are shown below

| | |
|---|--|
| $\text{C}_6\text{H}_5\text{CHO}$ | 1705 cm^{-1} [4] |
|  | 1700 cm^{-1} [16] |
|  | 1702 cm^{-1} [17] |
|  | 1698 cm^{-1} [17] 1687 cm^{-1} (nujol) [17] |

The carbonyl frequency is influenced by the number and position of substituents in the aromatic ring, the same way as in ketones (see below).

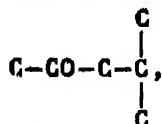
B. KETONES

1. Saturated Aliphatic Ketones

a. $\nu\text{C}=\text{O}$ vibration. In the vapor phase, saturated dialkylketones $\text{R}-\text{CO}-\text{R}$ have a strong absorption at 1738–1742 cm^{-1} [18]. In the liquid state or in solution (in nonpolar solvents such as carbon tetrachloride or carbon disulphide), the frequency decreases by 20–25 cm^{-1} . In the dialkyl ketones series, the mean $\nu\text{C}=\text{O}$ frequency is 1719 cm^{-1} [18–23]. In a large number of straight-chain aliphatic ketones $\text{R}-\text{CO}-\text{R}'$, where $\text{R}=\text{CH}_3$ and $\text{R}'=\text{methyl, ethyl, amyl}$, the absorption is constant in solution, occurring at 1719–1720 cm^{-1} [18, 22]. The decrease in frequency is very small on chain lengthening (e. g., in diamylketone $\nu\text{CO}=1716 \text{ cm}^{-1}$).

In dialkylketones branched in the α -position, the decrease in νCO frequency is very small (ca. 2–3 cm^{-1}), cf. the straight chain isomer [22]. Methylisopropyl ketone $\text{CH}_3\text{CO}-\text{CH}(\text{CH}_3)_2$ absorbs at 1719 cm^{-1} , whereas methyl-*n*-propyl ketone absorbs at 1720 cm^{-1} . In diisopropyl ketone, $(\text{CH}_3)_2\text{CH}-\text{CO}-\text{CH}(\text{CH}_3)_2$, the νCO frequency is 3 cm^{-1} lower than in di-*n*-propyl ketone (1716 cm^{-1}). The effect is somewhat stronger in pinacone $\text{CH}_3-\text{CO}-\text{C}(\text{CH}_3)_3$ which absorbs at 1711 cm^{-1} . Di-*tert*-butylketone $(\text{CH}_3)_3\text{C}-\text{CO}-\text{C}(\text{CH}_3)_3$ has the lowest frequency in this series (1687 cm^{-1}). This was explained by the change in force constant, due to steric compression exerted by the *t*-butyl group on the $>\text{C}=\text{O}$ angle. This compression also affects other physical

and chemical properties. Branching at a more remote position does not alter the νCO vibration; for example, a number of ketones,



have a normal absorption, at 1720 cm^{-1} [22].

Table II-135 shows characteristic frequencies and carbonyl intensities of some saturated alkyl ketones (in tetrachloroethylene) [23].

Unconjugated aromatic ketones with the CO group in the side-chain and separated from the aromatic ring by at least one CH_2 group have essentially the same frequencies as saturated dialkylketones. Benzylmethyl ketone $\text{C}_6\text{H}_5\text{CH}_2\text{CO}-\text{CH}_3$ absorbs at 1717 cm^{-1} and $\text{C}_6\text{H}_5(\text{CH}_2)_2\text{COCH}_3$ at 1723 cm^{-1} [23].

Table II-135 νCO frequencies and band intensities in dialkylketones

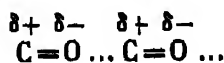
| Ketone | $\nu\text{CO}, \text{cm}^{-1}$ | $A, \text{cm}^2/\text{mole}$ |
|--|--------------------------------|------------------------------|
| CH_3COCH_3 | 1718 | 5.45 |
| $\text{CH}_3\text{COC}_2\text{H}_5$ | 1722 | 5.24 |
| $\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$ | 1721 | 5.25 |
| $\text{CH}_3\text{COCH}(\text{CH}_3)_2$ | 1719 | 5.09 |
| $\text{CH}_3\text{COC}(\text{CH}_3)_3$ | 1711 | 5.75 |
| $(\text{CH}_3)_2\text{CCOC}(\text{CH}_3)_3$ | 1687 | 4.75 |

These values correspond to spectra recorded in nonpolar solvents. In the liquid state, solid state, or vapor phase, changes in frequency are relatively large. When no hydrogen bonding with solvent takes place, shifts do not exceed 25 cm^{-1} . νCO frequencies of a number of saturated dialkylketones in the vapor phase and in nonpolar solvents are compiled in Table II-136. The frequency is practically the same in nonpolar solvents (CCl_4 , CS_2) as in the liquid state. A larger difference is observed between the vapor phase and the liquid state.

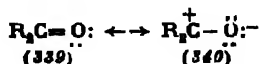
Table II-136 νCO frequencies of some ketones in vapor phase, liquid state, or solution

| Ketone | $\text{CO} (\text{cm}^{-1})$ | | |
|-----------------------|------------------------------|-------------|---------------------------------|
| | Vapor [28] | Liquid [18] | Solution in CCl_4 [22] |
| Acetone | 1742 | 1718 | 1719 |
| Methylethylketone | 1742 | 1721 | 1720 |
| Diethylketone | 1738 | 1720 | 1717 |
| Methyl-n-propylketone | 1737 | 1720 | 1720 |
| Dibutylketone | 1733 | 1718 | 1716 |
| Dodecylketone | 1740 | 1724 | 1717 |

The low frequency shift observed in the liquid state is attributed to association between ketone molecules.



The polar character of the CO group enables the occurrence of weak electrostatic bonds between the more positive carbon of one carbonyl group and the negatively polarized oxygen of another. Consequently, the contribution of structure (340) is increased. The C—O bond order is lowered. Hence the ν CO frequency decreases [24, 25].



A change in state from liquid to solid results not only in frequency shifts but also in appearance and disappearance of bands. Shifts due to the crystalline state are generally small and connected with intermolecular lattice forces.

Additional bands occurring in the crystalline state depend on the nature of the elementary cell. From this point of view the degree of dispersion (in mull or in nujol) is overimportant.

The disappearance of bands is connected with the disappearance of some molecular forms having a different symmetry than that in the crystal. Spectra of ketones in the liquid state or in solution show bands occurring from all the conformational isomers present. In the crystalline state supposed to have a single conformation, bands arising from unstable conformations disappear. Temperature dependence studies of spectra in solution have shown the existence of conformational isomers in diethylketone and a number of other ketones [26].

b. C—H Vibration. The carbonyl group affects the vibrations of CH groups in the α -position. The $-I$ or field effects of the C=O group result in characteristic changes both in CH frequency and band intensity.

CH stretching vibrations in CH_2 and CH_3 groups, activated by the neighboring carbonyl group, rise by ca. 25 cm^{-1} in the case of the asymmetric mode and by ca. 40 cm^{-1} in the case of the symmetric mode [27].

Figure II-84 shows the spectrum of methylethylketone in the ν CH and δ CH region. High-frequency shifts of the ν CH bands can be observed.

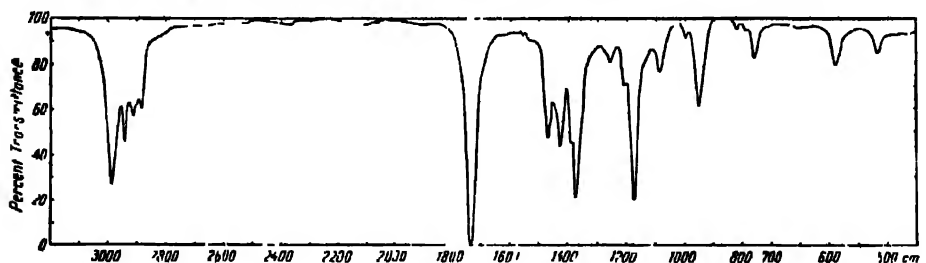


Fig. II-84 Infrared spectrum of methylethylketone

Much more characteristic, however, are shifts of bands arising from deformation modes. They enable the differentiation of these groups from other CH_2 or CH_3 groups in the molecule. The frequency of the δCH_2 scissoring vibration

falls from 1468 cm^{-1} (CH_2 in alkanes) to $1400\text{--}1430\text{ cm}^{-1}$ and the symmetric CH_2 deformation vibration falls from $1370\text{--}1380\text{ cm}^{-1}$ (CH_2 in alkanes) to $1355\text{--}1360\text{ cm}^{-1}$; for example, in methylethylketone the active methylene group ($-\text{CH}_2-\text{CO}-$) shows the scissoring vibration at 1414 cm^{-1} , whereas the CH_3 group absorbs at 1461 and 1360 cm^{-1} . These assignments are supported by deuteration. In $\text{CH}_3\text{CD}_2\text{COCOD}_2\text{CH}_3$ the CH_2 band at 1414 cm^{-1} disappears; in $\text{CD}_3\text{CH}_2\text{COCH}_2\text{CD}_3$ the CH_2 bands at 1461 and 1379 cm^{-1} disappear [28]. These shifts are of value in determining the degree of branching and the position of the CH_2 group.

2. Unsaturated ketones

a. $\nu\text{C}=\text{O}$ vibration.

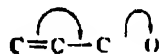
1. *Unsaturated ketones with isolated double bonds.* In unsaturated ketones with an isolated double bond, the $\text{C}=\text{O}$ and $\text{C}=\text{C}$ frequencies are the same as in the corresponding monofunctional compounds. The mean νCO frequency (in solution) is 1719 cm^{-1} and the mean intensity is $5.40\text{ cm}^2/\text{mole}$ [23] (Table II-137). Some interactions are, however, possible when the $\text{C}=\text{O}$ group is close in space to a double bond.

Table II-137 νCO and $\nu\text{C}=\text{C}$ frequencies and intensities in unsaturated ketones with isolated double bonds* [23]

| Formula | $\nu\text{C}=\text{O}$ | | $\nu\text{C}=\text{C}$ | |
|--|-----------------------------|---------------------------------|----------------------------|---------------------------------|
| | Frequency, cm^{-1} | A , cm^2/mole | Frequency cm^{-1} | A , cm^2/mole |
| $\text{CH}_3\text{COCCH}_2-\text{CH}=\text{CH}_2$ | 1723 | 5.24 | 1639 | 0.9 |
| $\text{CH}_3\text{COCH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$ | 1716 | 5.09 | 1631 | 1.17 |
| $\text{CH}_3\text{COCH}_2-\text{CH}=\text{C}=\text{CH}_2$ | 1719 | 5.29 | 1645 | 1.00 |
| $\begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_3 \\ \quad \\ \text{CH}_3\text{COCH}_2\text{C}=\text{CH}-\text{CH}_2 \end{array}$ | 1716 | 5.46 | 1670 | 0.11 |
| $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{COCH}_2-\text{CH}=\text{C}(\text{CH}_3)_2 \end{array}$ | 1718 1724 | 6.25 | 1683 | 0.25 |

* In tetrachloroethylene.

2. α , β -Unsaturated Ketones. Conjugation of the carbonyl group with

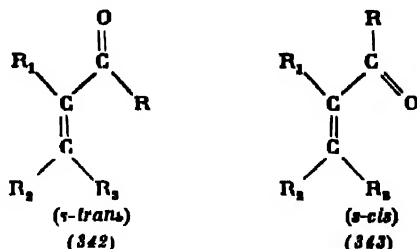


(34)

a double bond (34) results in a decrease in νCO frequency by ca. 40 cm^{-1} , cf. saturated ketones. Frequencies lie within the range $1665\text{--}1695\text{ cm}^{-1}$ [29–31].

Systematic studies of unsaturated ketones with various structures enabled some correlations between the frequency of the CO and $\text{C}=\text{C}$ groups and the structure or conformation of the α , β -unsaturated ketone [23, 32].

Theoretically aliphatic α , β -unsaturated ketones can exist in two planar conformations interconvertible by a 180° rotation about the C—C single bond linking the double bond to the carbonyl group.



In the *s-trans* conformation (342) the two double bonds are parallel to each other and in the *s-cis* conformation (343) they form an angle of 60° .

In unsaturated ketones where R₂ is hydrogen, both conformations are equally stable. When R₂ - alkyl, the *s-trans* conformation is sterically hindered by the interference of groups R and R₃. In this case the molecule adopts the *s-cis* conformation [23-33], which is preferred over a *quasi-trans* conformation [34]. In the latter case only a slight displacement of the two groups takes place. The two conformations differ in frequency and band intensity of the $\nu\text{C=O}$ and $\nu\text{C=C}$ vibrations [23, 32-35, 36]. Assignments were made by using some models with firmly established conformations based on elementary stereochemical arguments [23].

| Conformation | $\nu\text{C=O}$ cm^{-1} | Intensity, cm/mole |
|----------------------|----------------------------------|--------------------|
| <i>s-trans</i> (342) | 1680 | 9.0 |
| <i>s-cis</i> (343) | 1692 | 4.5 |

Cyclic α,β -unsaturated ketones with strain-free rings have undoubtedly an *s-trans* conformation. The mean $\nu\text{C=O}$ frequency is 1680 cm^{-1} and the intensity of the absorption is $9\text{ cm}^2/\text{mole}$.

Frequencies arising from the six-membered ring are very close to those of acyclic compounds and can be used as standards. Some values are compiled in Table II-138.

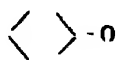
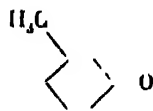
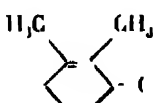
Cyclic α,β -unsaturated ketones with an exocyclic double bond (see Table II-139) have a firmly established *s-cis* conformation. The mean $\nu\text{C=O}$ frequency is slightly higher (1692 cm^{-1}) and the intensity appreciably smaller ($4.5\text{ cm}^2/\text{mole}$).

In both cases, compounds with alkyl-substituted double bonds have lower $\nu\text{C=O}$ and $\nu\text{C=C}$ frequencies.

In a large number of α,β -unsaturated ketones, $\nu\text{C=O}$ frequencies fall within this range. In a number of sterically unhindered ketones $\text{R}-\text{CO}-\text{CH}=\text{CH}_2$ or $\text{R}-\text{CO}-\text{CH}=\text{CH}-\text{R}$ with a *trans* double bond, where R=methyl,

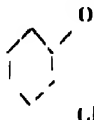
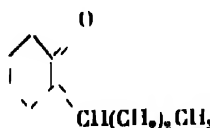
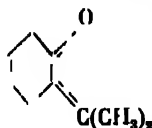
ethyl, *n*-propyl, or isopropyl [36--38], the $\nu_{\text{C=O}}$ absorption in solution shows a doublet due to an equilibrium between the *s-trans* and *s-cis* conformations (Table II-140).

Table II-138 $\nu_{\text{C=O}}$ and $\nu_{\text{C=C}}$ frequencies and intensities in ketones with *s-trans* conformation

| Ketone | $\nu_{\text{C=O}}$ | | $\nu_{\text{C=C}}$ | |
|--|--------------------------------|------------------------------------|--------------------------------|------------------------------------|
| | Frequency, cm^{-1} | A , cm^2/mole | Frequency, cm^{-1} | A , cm^2/mole |
|  -O | 1691 | 8.90 | 1621 | 0.03 |
|  O | 1680 | 9.45 | 1635 | 1.53 |
|  O | 1673 | 8.5 | 1635 | 1.87 |

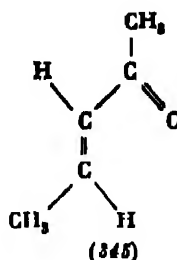
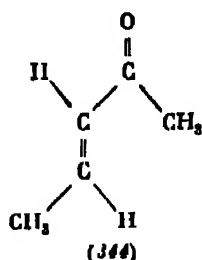
In the crystalline state, the spectrum shows a single absorption of the *s-trans* form. In solution, on increasing the temperature, bands arising from the *s-cis* form start appearing until equilibrium is reached.

Table II-139 $\nu_{\text{C=O}}$ and $\nu_{\text{C=C}}$ frequencies and intensities in ketones with *s-cis* conformation

| Ketone | $\nu_{\text{C=O}}$ | | $\nu_{\text{C=C}}$ | |
|--|-------------------------------|------------------------------------|--------------------------------|------------------------------------|
| | Frequency cm^{-1} | A , cm^2/mole | Frequency, cm^{-1} | A , cm^2/mole |
|  O CH ₂ CH ₂ | 1693 | 4.40 | 1622 | 4.08 |
|  O CH(CH ₂) ₂ Cl ₃ | 1692 | 4.51 | 1620 | 4.01 |
|  O C(CH ₃) ₂ | 1685 | 4.98 | 1611 | 3.51 |

Spectra of *trans*-3-pentenone-2 recorded in a mixture of tetrachloroethylene-chloroform between -10° and $+30^\circ\text{C}$ are shown in Fig. II-85. At -100°C

only bands assigned to the pure *s-trans* conformation (344) occur at 1674 cm^{-1} (νCO) and 1645 cm^{-1} ($\nu\text{C}=\text{C}$),



At higher temperatures, bands arising from the *s-cis* form (345) occur at 1693 cm^{-1} and 1630 cm^{-1} . The band intensity of the *s-trans* conformation

Table II-140 $\nu\text{C}=\text{O}$ and $\nu\text{C}=\text{C}$ frequencies and intensities in sterically un hindered α, β -unsaturated ketones (*s-trans* and mixtures) [23]

| Ketone | $\nu\text{C}=\text{O}$ | | $\nu\text{C}=\text{C}$ | |
|--|-------------------------------|------------------------------|-------------------------------|------------------------------|
| | Frequency cm^{-1} | A, cm^2/mole | Frequency cm^{-1} | A, cm^2/mole |
| $\text{CH}_3-\text{CO}-\text{CH}=\text{CH}_2$ | 1706 1686 | 1.93 | 1618 | 0.69 |
| $\text{CH}_3-\text{CO}-\underset{\text{CH}_3}{\text{C}}=\text{CH}_2$ | 1681 | 6.50 | 1630 | 0.68 |
| $\text{CH}_3-\text{CH}_2-\text{CO}-\text{CH}=\text{CH}_2$ | 1707 1690 | 1.80 | 1619 | 1.21 |
| $\text{CH}_3-\text{CO}-\underset{\text{H}}{\text{C}}=\underset{\text{H}}{\text{C}}-\text{CH}_3$ | 1701 1682 | 6.30 | 1634 | 1.91 |
| $\text{CH}_3-\text{CO}-\underset{\text{H}}{\text{C}}=\underset{\text{H}}{\text{C}}-\text{CH}(\text{CH}_3)_2$ | 1702 1683 | 6.68 | 1626 | 2.57 |
| $\text{CH}_3-\text{CO}-\underset{\text{C}_2\text{H}_5}{\text{C}}=\text{C}-\text{CH}_3$ | 1675 | 6.06 | 1642 | 1.31 |

is higher at -75°C than at $+30^\circ\text{C}$. At room temperature both sets of bands are present: νCO at 1693 and 1674 cm^{-1} and $\nu\text{C}=\text{C}$ at 1645 and 1630 cm^{-1} [32].

Sterically hindered α, β -unsaturated ketones with a *cis* alkenic double bond (interference of groups R and R₃ in structure (342)) adopt an *s-cis* conformation

(343). The spectrum shows a single $\nu\text{C}=\text{O}$ absorption at a mean frequency of 1692 cm^{-1} (the same as in cyclic ketones in Table II-139). Band intensities are low (ca. $4.5\text{ cm}^3/\text{mole}$) (Table II-141).

b. $\nu\text{C}=\text{C}$ vibration. The $\nu\text{C}=\text{C}$ frequency in α,β -unsaturated carbonyl compounds is lower than in nonconjugated compounds (Table II-142). Band intensities show large variations with structure [23, 39].

The highest frequency occurs in unsaturated nonconjugated ketones with an internal double bond (1675 cm^{-1}). Band intensity is, in turn, the lowest ($0.2\text{ cm}^3/\text{mole}$) because of the relatively symmetrical substitution of the double bond. When the double bond is terminal, the $\nu\text{C}=\text{CH}_2$ frequency decreases (1615 cm^{-1}) and the intensity rises ($1.0\text{ cm}^3/\text{mole}$; Table II-137).

Intensity variations of the $\nu\text{C}=\text{C}$ band in α,β -unsaturated ketones are large ($0.7\text{ cm}^3/\text{mole}$). If the conjugated double bond is terminal, a rise in frequency is observed (1625 cm^{-1}), whereas the intensity remains small ($0.75\text{ cm}^3/\text{mole}$). In compounds with an internal double bond, the type of substitution at this bond has a considerable influence on the $\nu\text{C}=\text{C}$ frequency. In ketones with a *trans*-disubstituted double bond the frequency is close to that in nonconjugated compounds with a terminal double bond (ca. 1635 cm^{-1}).

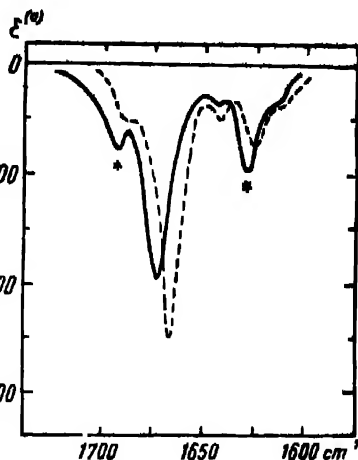
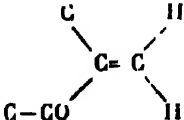
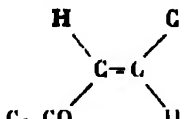
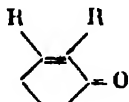
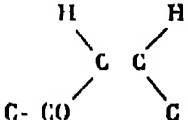
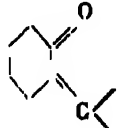


Fig II-85 Infrared spectrum of *trans*-3-pentenone 2 in a mixture of tetrachloroethylene - chloroform. Solid line at $+30^\circ\text{C}$; dotted line at -75°C . Stars show bands becoming weaker as the temperature is raised.

Table II-141 $\nu\text{C}=\text{O}$ and $\nu\text{C}=\text{C}$ frequencies in sterically hindered ketones (*s-cis* conformation)

| Ketone | $\nu\text{C}=\text{O}$ | | $\nu\text{C}=\text{C}$ | |
|---|-------------------------------|---------------------------------|-------------------------------|---------------------------------|
| | Frequency cm^{-1} | A , cm^3/mole | Frequency cm^{-1} | A , cm^3/mole |
| $\text{CH}_3-\text{CO}-\text{C}(\text{CH}_3)_2-\text{C}(\text{CH}_3)=\text{CH}_2$ | 1699 | 3.61 | 1618 | 2.30 |
| $\text{CH}_3-\text{CO}-\text{C}(\text{CH}_3)_2-\text{C}(\text{CH}_3)=\text{CH}-\text{C}(\text{CH}_3)_2$ | 1697 | 3.99 | 1616 | 2.87 |
| $\text{CH}_3-\text{CO}-\text{CH}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{CH}-\text{C}(\text{CH}_3)_2$ | 1693 | 3.88 | 1622 | 6.28 |
| $\text{CH}_3-\text{CO}-\text{C}(\text{CH}_3)_2-\text{C}(\text{CH}_3)=\text{CH}-\text{C}(\text{CH}_3)_2$ | 1696 | 4.45 | 1626 | 1.70 |
| $\text{CH}_3-\text{CO}-\text{C}(\text{CH}_3)_2-\text{C}(\text{CH}_3)=\text{CH}-\text{C}(\text{CH}_3)_2$ | 1689 | 1.95 | 1622 | 2.66 |

Table II-142 $\nu\text{C}=\text{C}$ frequencies in unsaturated ketones

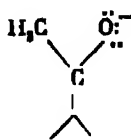
| Ketone | Frequency cm^{-1} | Δ cm^3/mole | Conformation |
|---|-------------------------------|---------------------------------------|--------------------------------|
| Unconjugated | | | |
| — internal double bond | 1675 | 0.2 | |
| — terminal double bond | 1645 | 1.0 | |
| Conjugated, sterically unhindered | | | |
| (C=C terminal)  | 1625 | 0.75 | <i>s-cis</i> <i>s-trans</i> |
| C=C <i>trans</i> alkenic  | 1635 | 2.0 | <i>s-cis</i> <i>s-trans</i> |
| endocyclic C=C  | 1635 | 1.87 | <i>s-trans</i> |
| Conjugated, sterically hindered | | | |
| C=C <i>cis</i> alkenic  | 1620 | 2-6 | <i>s-cis</i> |
| (C=C <i>cis</i> -ring)  | 1620 | ~4 | <i>s-cis</i> |

In contrast to the $\text{C}=\text{O}$ bond, the $\text{C}=\text{C}$ bond does not show differences between cyclic compounds with *s-trans* configuration and sterically unhindered compounds (Tables II-138 and II-140). The intensity rises to ca. $2.0 \text{ cm}^3/\text{mole}$. In sterically hindered ketones with *s-cis* conformation, the $\nu\text{C}=\text{C}$ frequency is lower than in compounds with *s-trans* conformation. However, the intensity varies within large limits 2-6 cm^3/mole . On the average it is $3.54 \text{ cm}^3/\text{mole}$ higher than in compounds with *s-trans* conformation. An exception is cyclohexanone (*s-trans*, cyclic) with the $\nu\text{C}=\text{C}$ frequency $=1621 \text{ cm}^{-1}$ and an extremely low intensity ($0.03 \text{ cm}^3/\text{mole}$) [23].

The $\Delta\nu$ value between $\nu\text{C}=\text{O}$ and $\nu\text{C}=\text{C}$ frequencies is indicative of the nature of the conjugated system. In sterically hindered compounds or in compounds with *s-cis* conformation, $\Delta\nu > 60 \text{ cm}^{-1}$ whereas in conjugated, sterically unhindered ketones or ketones with *s-trans* conformation, $\Delta\nu < 60 \text{ cm}^{-1}$ [23].

In *para*-substituted acetophenones (Table II-144), the highest frequency occurs in the nitro compound ($\nu_{\text{CO}}=1700 \text{ cm}^{-1}$) and the lowest, in the amino derivative (1677 cm^{-1}). Halogen atoms and the CH_3 group cause small shifts ($2-4 \text{ cm}^{-1}$) cf. acetophenone.

The direction and extent of frequency shifts are in agreement with the effect of substituents on electron distribution in the $\text{C}=\text{O}$ group. The CH_3 group, with a predominantly $+I$ effect acts in the same direction as the low $-I$ and $-E$ effects of the carbonyl group. A small decrease in frequency is observed. In the electron-donating NH_2 group, the strong $+E$ effect overshadows its weak $-I$ effect. Structure (349) with an appreciably lower C. O bond order is favored. Halogens, with a strong $-I$ effect and a weak $+E$ effect do not seem to influence the ν_{CO} frequency. In this case, the $-I$ and $+E$ effect of halogen atoms compensate the $-I$ and $-E$ effect of the carbonyl group. The relationship between bond order and electronic effects of R groups can be pointed out by relating the ν_{CO} frequency to the Hammett- σ constant of substituents [43] (Table II-144). The frequency falls for large negative σ values (-0.660) and rises for positive σ values ($+0.778$). The relationship is linear.



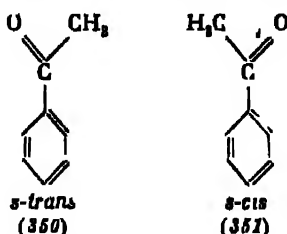
The existence of a relationship between the ν_{CO} frequency and the resonance energy has been shown [44, 45].

Table II-144 $\nu_{\text{C}=\text{O}}$ frequencies and intensities in substituted acetophenones [12]

| $\text{X}-\text{C}_6\text{H}_4-\text{CO}-\text{CH}_3$ | $\nu_{\text{CO}}, \text{cm}^{-1}$ | Intensity of integrated absorption $\text{l.mole}^{-1} \text{cm}^{-1} \cdot 10^{-1}$ | ϵ_{max} | Hammett- σ |
|---|-----------------------------------|---|-------------------------|-------------------|
| $\text{X}=\text{NH}_2$ | 1677 | 2.38 | 597 | 0.660 |
| OCH_3 | 1684 | — | — | -0.268 |
| CH_3 | 1687 | 2.44 | 685 | -0.170 |
| H | 1691 | 2.20 | 650 | 0.000 |
| F | 1692 | 2.17 | 656 | 0.062 |
| Cl | 1692 | 2.25 | 637 | +0.227 |
| Br | 1693 | 2.24 | 639 | +0.232 |
| I | 1693 | 2.39 | 709 | +0.276 |
| NO_2 | 1700 | 1.90 | 621 | +0.778 |

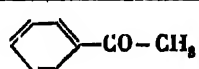
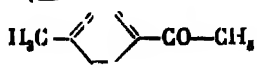
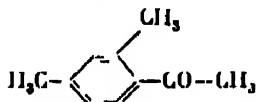
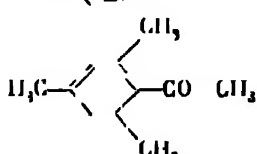
In *meta*-substituted acetophenones, variations in frequency are assigned primarily to the inductive effect. Band intensities are lower. A relationship between the frequency and the Hammett- σ constant has also been observed [42].

In addition to inductive $+I$ and conjugative $+E$ effects in *ortho*-substituted acetophenones, steric and field effects are also involved. The molecule can exist in *s-trans* form (350) and in *s-cis*-form (351).

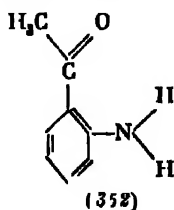


o-Methyl and 2, 3, 5, 6-tetramethylacetophenone have a single absorption, at 1690 cm^{-1} and 1701 cm^{-1} , respectively. It is assumed that in the tetramethyl derivative the COCH_3 group is not coplanar with the ring because of repulsion between the acetyl group and the *ortho*-methyl groups [12]. $\nu(\text{C}=\text{O})$ frequencies and absorption intensities in alkylacetophenones [23] are shown in Table II-145.

Table II-145 $\nu(\text{C}=\text{O})$ frequencies and absorption intensities in alkylacetophenones [23]

| Compound | $\nu(\text{C}=\text{O})\text{ cm}^{-1}$ | Intensity cm^2/mole |
|---|---|-------------------------------------|
|  | 1693 | 6.01 |
|  | 1689 | 6.56 |
|  | 1684 | 7.13 |
|  | 1705 | 6.80 |

In carbon tetrachloride solution, *o*-chloro-, *o*-bromo- and *o*-nitroacetophenones show two bands as a result of an assumed equilibrium between *s-cis* (351) and *s-trans* (356) structures [12]. The higher frequency band of the doublet was assigned to the *cis* isomer and lower one to the *trans* isomer. At lower temperatures the higher frequency band becomes stronger; consequently, the absorption corresponds to the thermodynamically more stable isomer (*s-cis*).



The spectrum of *o*-fluoroacetophenone shows a single band at 1692 cm^{-1} corresponding to the lower frequency isomer (*s-trans*) in *o*-chloro- and *o*-bromoacetophenones. Shifts in this frequency show that on increasing the size of the halogen atom, the *s-cis* conformation becomes predominant. This was assigned to an *ortho*-effect.

In *o*-aminoacetophenone (352), the intramolecular hydrogen bond in the *s-cis* conformation results in a decrease in νCO frequency to 1653 cm^{-1} (see chelate compounds of hydroxyketones).

c. **Diaryl ketones.** The presence of two aryl groups in diaryl ketones results in a decrease in νCO frequency to 1664 cm^{-1} (benzophenone in CCl_4)

Table II-146 νCO frequencies in *para*-substituted benzophenones [22]

| R | $\text{R}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{R}'$ $\nu\text{CO}, \text{cm}^{-1}$ | Hammelt- σ |
|---------------------------|--|-------------------|
| $\text{N}(\text{CH}_3)_2$ | $\text{N}(\text{CH}_3)_2$ | 1639 |
| NH_2 | H | 1651 |
| OCH_3 | OCH_3 | 1655 |
| CH_3 | CH_3 | 1659 |
| OCH_2 | H | 1658 |
| $\text{C}(\text{CH}_3)_3$ | H | 1664 |
| C_6H_5 | H | 1661 |
| H | H | 1664 |
| F | H | 1667 |
| Br | H | 1665 |
| Cl | Cl | 1670 |

* Reference 43.

[18, 21, 22] (Table II-146). As in acetophenones the substituents affect the vibration of the carbonyl group. Relationships between the νCO frequency

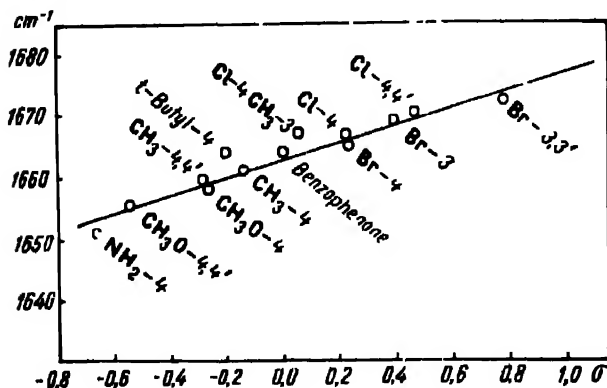


Fig. II-86 Variation of the νCO frequency with the Hammett- σ constant in substituted benzophenones

and a number of physical, thermodynamic, and kinetic constants have been found [22]; for instance, there is a linear relationship between the νCO frequency in *para*-substituted benzophenones and the Hammett- σ constant (Fig. II-86).

In phenylcycloalkyl ketones (e. g. cyclobutyl-, cyclopentyl-, and cyclohexylphenylketone), the νCO frequency is 1686

1687 cm^{-1} [22]. Phenyl-

cyclopropylketone has a lower frequency, 1677 cm^{-1} , close to that of α, β -unsaturated phenylketones ($\text{C}_6\text{H}_5\text{CO}-\text{CH}=\text{CH}-\text{CH}_3$ absorbs at 1680 cm^{-1}). A styryl instead of a phenyl group raises the frequency by ca. 5 cm^{-1} [22].

4. Mono- and polycyclic ketones

In *monocyclic saturated* ketones, the νCO frequency varies with ring size [46–48]. In cyclanones with three- to eight-membered rings, the frequency decreases in the order:

$$C_3 > C_4 > C_5 > C_6 > C_7 \approx C_8.$$

νCO frequencies of ketones with 4- to 8-membered rings recorded in carbon tetrachloride solution are shown in Table II-147 [49, 50].

Table II-147. νCO frequencies in cyclic ketones (10% solution in CCl_4)

| Ketone | $\nu\text{CO}, \text{cm}^{-1}$ | νCO calculated | ϕ degrees |
|----------------|--------------------------------|------------------------------|----------------|
| Cyclobutanone | 1788 | 1791 | 82 |
| Cyclopentanone | 1746 | 1750 | 101 |
| Cyclohexanone | 1715 | 1717 | 116 |
| Cycloheptanone | 1703 | 1704 | 121 |
| Cyclooctanone | 1702 | 1701 | 133 |

Frequencies of six-membered ring ketones are close to those of aliphatic saturated ketones (1720 cm^{-1} in acetone). The frequency rises by ca. 10 cm^{-1} in the five-membered ring [51] and by ca. 60 cm^{-1} in the four-membered ring. For cyclopropanone (obtained from ketone and diazomethane), a band at 1825 cm^{-1} was assigned. However, the assignment is uncertain since the spectra were recorded on a crude product [52, 52 a].

A rise in νCO frequency with decreasing ring size was assigned to changes in hybridization in small rings [53]. In smaller rings the ring bonds become enriched in *p*-component and the carbon-oxygen bond becomes enriched in *s*-component. This corresponds to a larger force constant resulting in a rise in νCO frequency.

A number of reliable correlations have been established between the frequency of the carbonyl group and some physical and chemical properties of cyclic ketones. Thus shifts in CO frequency in various cycloalkane rings have been correlated with the deformation of the $>\text{C}=\text{O}$ angle between $\text{C}-\text{C}$ bonds. The following empirical formula has been proposed [54]:

$$\nu(\text{cm}^{-1}) = 1278 + 68 \alpha - 2.2 \phi.$$

This formula enables the determination of angle $\phi(>\text{CO})$ in degrees in a number of simple cyclic ketones [47] (α is the force constant of the $\text{C}=\text{O}$ bond in dialkyl ketones expressed in 10^{-8} dyne/cm ; consequently, in the above relation $\alpha = 10.2 \pm 0.3$) (see Table II-148). The values obtained are shown in Table II-147. Since α values are not accurate, these figures have only a comparative value. The errors are $\pm 9^\circ$. Similar results have been obtained by other workers as well [50, 55]. It has been shown that angles in cyclobuta-

none are not equal (Fig. II-87) which means that the conformation of the molecule is nonplanar [56]. The high νCO frequency in cyclobutanone was attributed [57] to a mechanical rather than an electronic effect [49, 53] (see below).

The C=O frequency is sensitive both to electronic and mechanic (coupling) effects. Therefore, the force constant was proposed as a comparative criterion for the evaluation of the nature of the C=O bond [57]. The calculated values for k [51, 57] have been related to the main effects influencing νCO shifts in a large number of ketones (see Table II-148).

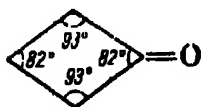


Fig II-87 Geometry of the cyclobutanone molecule.

According to these calculations, the C=O bond in cyclobutanone has approximately the same force constant ($10 \cdot 3 \cdot 10^5$ dyn/cm) as in open-chain saturated ketones. The authors consider that the rise in frequency is due to

the fact that in the four-membered ring the angle between the C=O bond and the adjacent C—C bond is smaller than in normal ketones. This geometry enhances the possibility of coupling between the adjacent C=O and C—C oscillators.

Table II-148 νCO frequencies in ketones [57]

| Carbonyl compound | $k \cdot 10^5$ dyn/cm | $\nu\text{CO cm}^{-1}$ | Predominant effect |
|---------------------|-----------------------|------------------------|--|
| Saturated ketones | 10 - 10.5 | 1706 - 1725 | |
| Unsaturated ketones | 9 - 9.8 | 1650 - 1750 | Conjugative |
| Halogenated ketones | 10.3 - 10.9 | 1725 - 1765 | Inductive |
| Cyclobutanone | 10.3 | 1775 | Vibrational coupling |
| Quinones | 9.5 - 9.9 | 1660 - 1690 | Vibrational coupling + inductive, conjugative effect |

Consequently, the rise in νCO frequency in cyclobutanone is associated with a mechanical and not an electronic effect [57, 57a].

As in open-chain ketones, the carbonyl frequency in cyclanones is approximately the same in the liquid phase as in solutions in nonpolar solvents. In the vapor phase it rises by 20 - 25 cm^{-1} .

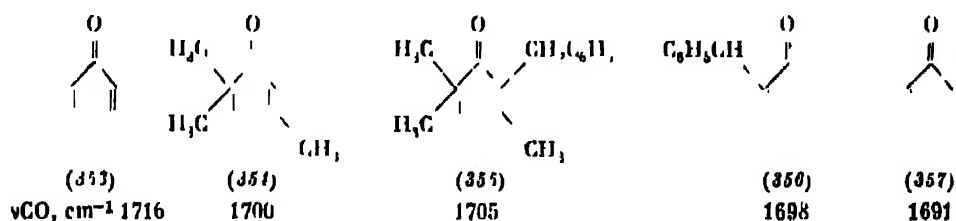
Cyclohexanone absorbs at 1715 cm^{-1} in carbon tetrachloride solution and at 1712 cm^{-1} in the vapor phase [18, 58]. In a large number of six-membered ring ketones, the νCO frequency recorded in carbon tetrachloride solution lies in the range 1710 - 1720 cm^{-1} [16].

Frequencies in cyclopentanone and other five-membered ring ketones are 30 - 40 cm^{-1} higher than in strain-free rings (see Table II-147). In cyclopentanone the νCO frequency is 1746 cm^{-1} in solution and 1750 cm^{-1} in the liquid state [18, 58]. The carbonyl band in cyclopentanones is doubled [59], the two components occurring at 1730 and 1750 cm^{-1} [60]. Various explanations have been proposed for this splitting [46, 59, 60]. Most likely it is due to a Fermi resonance [59 - 61].

The ν_{CO} frequency in cycloheptanone and cyclooctanone is slightly lower than in cyclohexanone [18, 58]; the decrease in frequency was explained by a hybridization effect [18].

On raising the temperature to $+85^{\circ}\text{C}$, the carbonyl band in cyclooctanone ($1689\text{--}1711\text{ cm}^{-1}$) shows a shoulder at 1730 cm^{-1} , assigned to a conformational isomer [62].

In α, β -unsaturated ketones the ν_{CO} frequency decreases by ca. $35\text{--}40\text{ cm}^{-1}$ cf. the corresponding saturated compounds [46, 63, 64]. Cyclopentenone (353) absorbs at 1716 cm^{-1} [18]. In trimethyl derivatives (354) and (355) conjugation of the carbonyl with endocyclic and exocyclic double bonds results in a fall in ν_{CO} frequency to 1698 cm^{-1} .

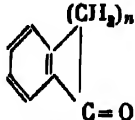


The same effect is observed in α, β -unsaturated cyclohexenones, absorbing in the range $1664\text{--}1691\text{ cm}^{-1}$ [66]. Cyclohexenone (357) with an *s-cis* conformation absorbs at 1691 cm^{-1} and *trans*-2-cycloheptenone and 2-cyclooctenone absorb at 1712 cm^{-1} [66a].

Strained cyclopropanone absorbs at 1855 cm^{-1} [66b]. In compounds substituted with CH_3 groups, the ν_{CO} frequency decreases to the bottom of the range (some compounds are shown in Table II-138 and have been discussed along with open-chain α, β -unsaturated ketones).

In benzocyclanones ν_{CO} frequencies vary with ring size [64]. A decrease in frequency in the series α -indanone, α -tetralone, α -benzosuberone has been observed [64, 67]. ν_{CO} frequencies in some benzocyclanones of type (358), where $n=2\text{--}9$ are shown in Table II-119.

Table II-119 ν_{CO} frequencies (cm^{-1}) in benzocyclanones and cyclanones*

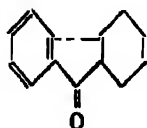
| Benzocyclanone | n | Number of ring atoms | Benzocyclanone | | Cyclanone |
|--|---|----------------------|--------------------|--------------------------|-----------|
| | | | ν_{exp} | ν_{calc}^{**} | |
|  (358) | 2 | 5 | 1723 | 1718 | 1751 |
| | 3 | 6 | 1681 | 1662 | 1715 |
| | 4 | 7 | 1676 | 1671 | 1704 |
| | 5 | 8 | 1667 | 1669 | 1702 |
| | 9 | 12 | 1685 | — | — |
| | | | | | |

* Liquid.

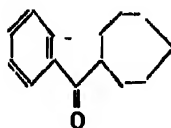
** Obtained by subtracting 33 cm^{-1} (conjugative effect) from the corresponding values in cyclanones.

Conjugation with the benzene ring results in a decrease in frequency of ca. 33 cm^{-1} . Shifts in frequency are assigned to the hybridization effect [68].

For more complex cyclic ketones (359) and (360) where the five-membered ring is condensed with a six-membered ring (359), the νCO frequency is 1715 cm^{-1} , and in compound (360) with a seven-membered ring, the frequency is 1706 cm^{-1} [69].



(359)



(360)

5. Bi- and polycyclic bridged ketones

a. νCO Vibration. The νCO frequency in bi- and polycyclic ketones is determined by ring size, the same way as in monocyclic ketones [47, 48]. In strain-free systems the frequency is slightly higher than in the corresponding monocyclic ketone. In strained systems the frequency rises and varies with the position of the carbonyl group. The highest values ($1770\text{--}1780\text{ cm}^{-1}$) are recorded in bridged bicyclic compounds such as bicycloheptanone-7 (see Table II-150) [70, 76]. These high frequencies, comparable to those in the four-membered ring, are probably due to rehybridization imposed by ring strain.

Characteristic νCO frequencies of some bi- and tricyclic systems are shown in Table II-150.

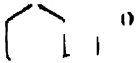
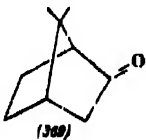



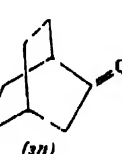
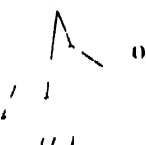
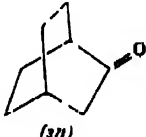
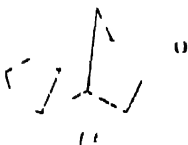


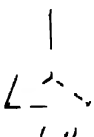
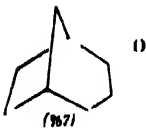
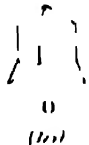
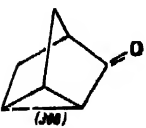
Carbonyl frequencies in these systems have been used to evaluate the deviation of bond angles and thus to establish the geometry of the molecule [17, 63]. In compound (373) the low frequency corresponds to a carbonyl group conjugated with the adjacent aromatic ring. The C—O frequency in tricyclo [2.2.2.0^{2,6}] octanone-3 (374) is due to conjugation with the cyclopropane ring [76].

b. C—H Vibrations. Vibrations of the CH_2 group adjacent to the carbonyl group can differ from those of other methylene groups in the ring.

In cyclanones with 6–11 carbon atoms [77], νCH_2 vibrations of methylene groups adjacent to the carbonyl have higher frequencies. The sym νCH_2 absorption occurs at $2860 \pm 20\text{ cm}^{-1}$ and the asym νCH_2 band occurs at $2930 \pm 30\text{ cm}^{-1}$. Cyclopentanone is an exception, absorbing at 2885 and 2965 cm^{-1} , respectively. Deuteration has shown that in cycloheptanone and cyclohexanone the asym νCH_2 band is shifted by 25 cm^{-1} toward higher frequencies as compared to the other methylene groups in the ring; the sym νCH_2 frequency shifts still further away, by 40 cm^{-1} [77].

δCH_2 deformation (scissoring) vibrations of the same methylene groups decrease to such an extent that they can be readily distinguished from the deformations of other CH_2 groups in the ring. Also, the bands become considerably stronger. Absorptions of $\alpha\text{-CH}_2$ groups occur at $1403\text{--}1435\text{ cm}^{-1}$ cf. $1452\text{--}1460\text{ cm}^{-1}$ for the normal ring methylene groups.

Table II-150 ν_{CO} frequencies in bi- and polycyclic systems

| Compound | No of ring atoms | ν_{CO} cm^{-1} | References | Compound | No of ring atoms | ν_{CO} cm^{-1} | References |
|---|------------------|------------------------------------|------------|---|------------------|------------------------------------|------------|
|  | 4 | 1780 | [71] |  | 5 | 1764 | [53] |
|  | 5 | 1739 | [72] |  | 5 | 1770 | [55] |
|  | 4 | 1751 | [47] |  | 6 | 1757 | [50] |
|  | 3 | 1736 1724 | [73] |  | 5 | 1740 | [74] |
|  | 5 | 1750 | [47] |  | 6 | 1700 | [75] |
|  | 5 | 1748 | [47] |  | 6 | 1735 | [76] |
|  | 6 | 1731 | [47] |  | 6 | 1745 | [50] |
|  | 5 | 1768 1731 | [17] | | | | |

Absorptions in the 1400–1460 cm^{-1} region for ketones with 4–17 membered rings are shown in Table II-151.

Table II-151 δCH_2 frequency in cyclanones [78]

| Ketone | CH_2 cm^{-1} | | $\alpha\text{-CH}_2$ cm^{-1} |
|-----------------------|-----------------------------------|------|--|
| Cyclobutanone | 1156 | | 1405* |
| Cyclopentanone | 1460 | 1449 | 1403 |
| Cyclohexanone | 1414 | 1423 | |
| Cycloheptanone | 1118 | 1439 | 1406 |
| Cyclooctanone | 1163 | 1441 | 1409 |
| Cyclononanone | 1406 | 1442 | 1430 |
| Cyclodecanone | 1169 | 1451 | 1440 1413 |
| Cyclododecanone | 1465 | 1453 | 1441 1411 |
| Cyclotetradecanone | 1457 | 1437 | 1407 |
| Cyclohexadecanone | 1450 | 1434 | 1402 |
| Cycloheptadecanone | 1450 | 1438 | 1400 |
| Cyclodecanedione-1, 6 | 1142 | | 1418** |

* [56].

** [79].

The number and position of δCH_2 bands in cyclanones depends on ring size and conformation, the same as in cyclic hydrocarbons [87] (see Cycloalkanes). The 1400–1410 cm^{-1} bands are assigned to the active methylene group in the α -position.

6. Quinones

Quinones are a special case of α, β -unsaturated ketones. Characteristic frequencies in this class of compounds arise from $\text{C}=\text{O}$ and $\text{C}=\text{C}$ groups and lie in the range 1587–1695 cm^{-1} . The stronger, higher frequency band was assigned to the carbonyl group.

a. $\nu\text{C}=\text{O}$ Vibrations. *p*-Quinones with the two carbonyl groups in the same ring (e.g. *p*-benzoquinones) absorb in the range 1660–1680 cm^{-1} [80–82, 82a]. In larger quinoid systems (e.g. *amphi*-quinones or polycyclic quinones), the νCO frequency is lower, occurring at 1635–1655 cm^{-1} [83–85].

A particularly low frequency (1626 cm^{-1}) has been found in 4,4'-diphenoquinone [83].

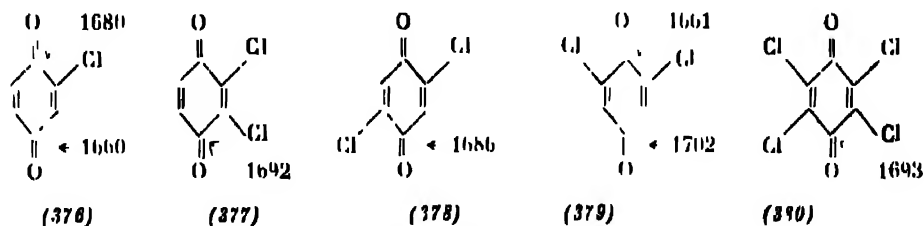
In some quinones the carbonyl band is doubled. The reason for this doubling has been interpreted in several ways [36], namely vibrational coupling (by analogy with peroxides and anhydrides) [87], intramolecular vibrational effect [88], and separation of unperturbed frequencies of νCO stretching vibrations due to steric or electronic effects [82, 89].

Benzoquinone was assigned a single band in earlier works. Actually it shows a doublet which remained unnoticed because of poor experimental conditions.

The frequency, intensity, and splitting of the $\nu(\text{C})$ band in substituted *p*-benzoquinones are influenced by the nature, position, and number of substituents.

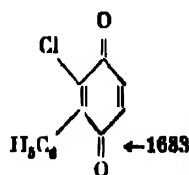
Electron-donating groups ($+I$ effect, alkyl groups) or groups with a $-I$ but $+E$ effect (methoxyl, hydroxyl) lower the frequency. The effect is enhanced by an increased number of substituents of this type. The hydroxyl group shows the most powerful effect [80, 81]. Electronegative substituents with $-I$, $-E$ effects raise the frequency [80]. Also in this case the shift depends on degree of substitution [90, 91]. *p*-Benzoquinone substituted with a chlorine atom (with a strong $-I$ and $+E$ effect) (376), shows two νCO bands [80, 82]. The relative intensity of the two absorptions depends on the polarity of the solvent [89]. The distance $\Delta\nu$ (cm^{-1}) between the two bands is 20 cm^{-1} . In 2-chloroquinone the two absorptions have frequencies of 1680 and 1660 cm^{-1} . The higher frequency band was assigned to the carbonyl group next to the halogen atom, perturbed by a field effect as in halo ketones. The second band corresponds to the carbonyl group adjacent to a hydrogen atom.

This interpretation is supported by the fact that 2, 3-dichloroquinone (377) and 2, 5-dichloroquinone (378) show a single band at 1692 and 1688 cm^{-1} , respectively, whereas 2, 6-dichloroquinone (379) shows two bands, at 1702 cm^{-1} and 1661 cm^{-1} ($\Delta\nu=41 \text{ cm}^{-1}$). Chloranil (380) with chlorine atoms in the 2-, 3-, 5-, 6-, positions shows a single band at 1693 cm^{-1} . The same effects take place in the corresponding bromoquinones. Monobromobenzoquinone, absorbing at 1682 cm^{-1} is an exception [82]. This may be either because of a diminishing field effect in the order $\text{Cl} > \text{Br} > \text{I}$ or, more likely, because of superimposition of the two bands (2, 6-dibromoquinone shows two bands, at

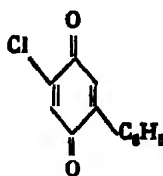


1703 and 1663 cm^{-1} , $\Delta\nu=40 \text{ cm}^{-1}$) [82]. A phenyl substituent does not alter the frequency of the carbonyl group in quinones. 2-Phenyl-*p*-benzoquinone shows a band at 1671 cm^{-1} with an inflection at 1663 cm^{-1} . In phenylchloro-*p*-benzoquinones, the shifts depend on the relative positions of the two substituents. Disubstituted compounds with substituents in the 2- and 3- position (381) or 2- and 5- position (382) show a single $\nu\text{C}=\text{O}$ band. Compounds disubstituted in the 2- and 6- position (383), where substituents are adjacent to a single carbonyl group, show two bands [82].

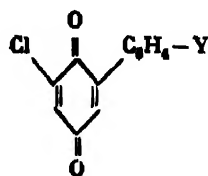
It is believed that in compounds (381) and (382) the opposite effect of the two substituents reduces the distance between the two bands to the extent



(381)



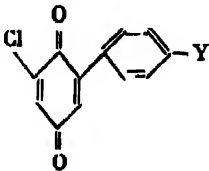
(382)



(383)

that they overlap. The spectrum shows a single absorption at 1683 cm^{-1} . In compound (383) the frequency and distance between the two components of the doublet are also influenced by substituents in the *para*-position of the benzene ring (Table II-152).

Table II-152 νCO frequencies in substituted quinones [82]

|  | | | |
|---|--------------------------------|------|-----------------------------|
| Y | $\nu\text{CO}, \text{cm}^{-1}$ | | $\Delta\nu, \text{cm}^{-1}$ |
| H | 1688 | 1659 | 29 |
| Cl | 1685 | 1658 | 27 |
| NO_2 | 1682 | 1657 | 25 |

In 2,6-dichloro-5-*p*-nitrophenyl-*p*-benzoquinone, the splitting is 35 cm^{-1} (νCO occurs at 1698 and 1663 cm^{-1}). Frequencies of halogenoaryl-*p*-benzoquinones substituted in the 2- and 5-positions are $5\text{--}9\text{ cm}^{-1}$ lower (1674 cm^{-1}) than in 2,3-disubstituted isomers (1683 cm^{-1}). This is of value for the determination of the mode of substitution.

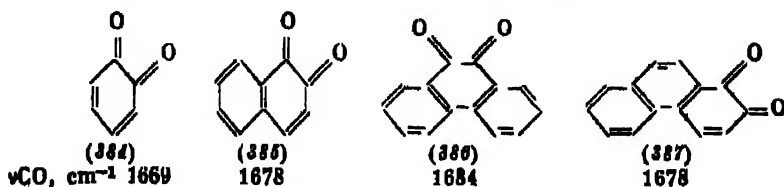
1,4-Naphthoquinone absorbs at 1675 cm^{-1} and 9,10-anthraquinone absorbs at 1678 cm^{-1} [84].

b. Other vibrations in quinones. Out-of-plane C—H deformation vibrations in *p*-benzoquinones have the following frequencies, depending on the mode of substitution:

| | |
|--|--|
| monosubstituted <i>p</i> -benzoquinones | 825–865 and 901–916 cm^{-1} , |
| 2,3-disubstituted <i>p</i> benzoquinones | 841–846 cm^{-1} , |
| 2,5- and 2,6-disubstituted <i>p</i> -benzoquinones | 897–920 cm^{-1} . |

c. $\nu\text{C}=\text{C}$ vibrations. The frequency of the $\nu\text{C}=\text{C}$ skeletal vibration is ca. 1600 cm^{-1} . In substituted compounds the intensity of the absorption is strongly influenced by the nature of the substituent. In methoxyquinones the band is stronger than in the corresponding methyl- or hydroxyquinones [81, 82].

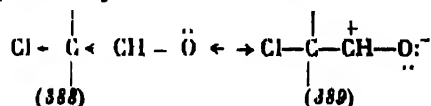
Frequencies of *o*-quinones lie in the range $1669\text{--}1684\text{ cm}^{-1}$ [84] and cannot be differentiated from those of *p*-quinones [92].



C. SUBSTITUTED CARBONYL COMPOUNDS

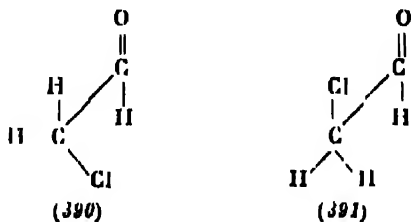
1. α -Halogenoaldehydes

α -Halogenoaldehydes have been less extensively studied than α -halogeno-ketones. The electronegative halogen atom attracts the electrons of the $\text{C}=\text{O}$ group reducing its polarity. Contribution of structure (388) is greater than (389) and the band order rises, cf. unsubstituted aldehydes. The frequency of the carbonyl group rises by ca. $10\text{--}15\text{ cm}^{-1}$



Monochloroacetaldehyde shows a ν_{CO} absorption at 1752 cm^{-1} in the vapor phase, at 1758 cm^{-1} in carbon tetrachloride solution, and at 1758 cm^{-1} in acetonitrile solution [93]. On increasing the number of halogen atoms in the α -position the frequency rises substantially. In the vapor phase trichloroacetaldehyde Cl_3CCHO absorbs at 1778 cm^{-1} , the shift being $+26\text{ cm}^{-1}$, cf. monochloroacetaldehyde. In carbon tetrachloride solution the frequency is 1768 cm^{-1} .

The occurrence of a single absorption band in spectra of halogenoacetaldehydes in the vapor phase as well as in the liquid phase or in solution suggests that these molecules adopt a single conformation. The infrared spectrum of monochloroacetaldehyde indicates two possible conformations, one with the chlorine and oxygen atoms *anti*-staggered (390) and the other *syn*-eclipsed (391) (*cis*). The first one is favored. In conformation (391) with the oxygen atom adjacent (eclipsed) by the chlorine atom, the $\nu_{\text{C}-\text{O}}$ frequency should be appreciably higher because of electrostatic repulsion between the chlorine and oxygen atoms. Consequently, it is believed that the molecule adopts a conformation in which chlorine and oxygen are in the most remote position (*anti*) (390)

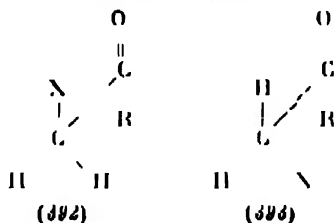


2. α -Halogenated Ketones

In α -chloro and α -bromo ketones the carbonyl frequency is 20 cm^{-1} higher than in the corresponding nonhalogenated ketones. In fluoroketones [95] it is 40 cm^{-1} higher. The strongly electronegative halogen atom alters the electron distribution in the CO group both by its $-I$ effect and field effect (electrostatic effect transmitted through space) which in this case is very important. Consequently the geometry of the molecule plays a predominant role, and shifts in frequency in conformational isomers are to be predicted.

The first correlations between the νCO frequency and the nature, position, number, and steric orientation of the halogen atoms have been observed in ketosteroids with a rigid ring system [96, 110]. In a number of 2-bromo- or 4-bromo-3-ketosteroids, a rise in νCO frequency of about 20 cm^{-1} has been observed (1735 cm^{-1}), cf. the corresponding nonhalogenated 3-ketosteroid ($1715\text{--}1719\text{ cm}^{-1}$). It was also shown that when the carbonyl group is adjacent to two bromine atoms $-\text{CHBr}-\text{CO}-\text{CHBr}-$ the $\Delta\nu\text{CO}$ shift is almost double; for example, 2,1-dibromo-3-ketosteroids absorb at 1760 cm^{-1} . If the two bromine atoms are at the same carbon atom $-\text{CO}-\text{CBr}_2-$, the effect is no longer additive. 2-Bromocholestanone-3 and 2,2-dibromocholestanone-3 have the same νCO frequency ($1735\text{--}1739\text{ cm}^{-1}$). This behavior was explained by the different influence of axial and equatorial halogen atoms on the νCO vibration (see Halogenocyclanones).

A more careful study of α -halogenoketones shows that the carbonyl frequency depends to a great extent on the conformation of the molecule. In the case of ketones $\text{R}-\text{CO}-\text{CH}_2\text{X}$, the halogen and oxygen atoms can be close in space in a *syn*-eclipsed (*cis*) conformation (392) or remote from each other in an *anti*-staggered conformation (393)



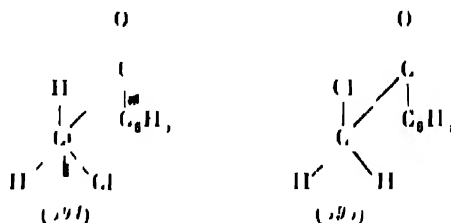
Factors determining the stability of one or the other conformational isomer under given conditions are electrostatic repulsion between chlorine and oxygen (both atoms are electronegative) and steric repulsion between the chlorine atom and the group R attached to the carbonyl group. Depending on which effect predominates, the molecule will adopt either the conformation (393) or the more polar conformation (392). In conformation (392) the halogen atom increases the $\text{C}=\text{O}$ bond order through a dipolar field effect. The $-I$ effect acts in the same direction. In conformation (393) the two effects act in opposite directions and compensate each other to a great extent. In the infrared spectrum the carbonyl frequency will be higher in conformation (392) and practically unchanged in conformation (393).

These criteria have been used in the identification of stable conformations of many acyclic ketones in various physical states. From this it became possible to evaluate the factors determining the stability of conformational isomers; for example, in ω -chloroacetophenone [97] in the crystalline state, the νCO frequency rises by 20 cm^{-1} (1702 cm^{-1}) cf. acetophenone (1682 cm^{-1}) (Table II-153).

Table II-153 νCO frequencies in ω -chloroacetophenones [98]

| Ketone | $\nu\text{CO}, \text{cm}^{-1}$ | | | | |
|---|--------------------------------|------------|-------|----------------------------|------------------------------------|
| | Vapor | Liquid | Solid | Solution in CCl_4 | Solution in CH_3CN |
| $\text{C}_6\text{H}_5-\text{CO}-\text{CH}_3$ | 1709 | 1687 | 1682 | 1692 | 1688 |
| $\text{C}_6\text{H}_5-\text{CO}-\text{CH}_2\text{Cl}$ | 1709 | 1693, 1709 | 1702 | 1696, 1715 | 1696, 1710 |
| $\text{C}_6\text{H}_5-\text{CO}-\text{CHCl}_2$ | 1707, 1729 | 1690, 1707 | 1709 | 1692, 1716 | 1695, 1713 |
| $p\text{-Cl}-\text{C}_6\text{H}_4-\text{CO}-\text{CH}_2\text{Cl}$ | 1709 | 1695, 1707 | 1708 | 1698, 1715 | 1695, 1711 |

In the liquid state or in solution a doublet occurs, attributable to the existence of two conformational isomers (394) and (395); in the vapor phase there is a single absorption equal to that in acetophenone.



The higher frequency νCO band in the crystalline state (1702 cm^{-1}) can be assigned to the more stable conformation (395). It corresponds to the 1682 cm^{-1} frequency in acetophenone. In the vapor phase the stable conformation is (394) (*anti*-staggered), absorbing at 1709 cm^{-1} . Consequently, the lower frequency band in the liquid state or in solution (1683 cm^{-1}) corresponds to conformation (394) and the higher band to conformation (395). Dichloroacetophenone has two νCO absorptions in the vapor phase: 1707 and 1729 cm^{-1} . Consequently, the second halogen atom contributes to the stabilization of a more polar form of higher frequency (1729 cm^{-1}).

Table II-151 shows νCO frequencies of several α -mono- and polychloro-ketones [98]. It can be seen that at least two νCO bands occur in solution, arising from conformational isomers. In the vapor phase a single conformational isomer is present (with the exception of asymmetric dichloroacetone).

In the case of monochloroacetone, dipole moment measurements and spectroscopic methods have shown that the stable form in the liquid and solid state is the more polar conformation (396) (Cl and O *cis*). Conformation (397) (*anti*-staggered) is favored in vapor phase.

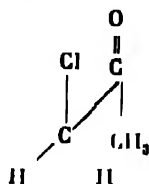
Table II-154 ν CO frequencies in α -chloroketones

| Ketone | ν CO, cm^{-1} | | | | |
|---|----------------------------|------------------|------------------|----------------------------|------------------------------------|
| | Vapor | Liquid | Solid | Solution in CCl_4 | Solution in CH_3CN |
| $\text{CH}_3\text{—CO—CH}_3$ | 1738 | 1715 | — | 1719 | 1715 |
| $\text{CH}_3\text{—CO—CH}_2\text{Cl}$ | 1743 | 1725, 1743 | 1725, 1742* | 1726, 1752 | 1726, 1744 |
| $\text{CH}_3\text{—CO—CHCl}_2$ | 1722, 1756 | 1740 | 1732 | 1721, 1743 | 1716, 1745 |
| $\text{CH}_2\text{Cl—CO—CH}_2\text{Cl}$ | 1746 | 1728, 1742, 1755 | 1745 | 1730, 1746 | 1711, 1752 |
| $\text{CHCl}_2\text{—CO—CHCl}_2$ | 1770 | 1762, 1773 | 1739, 1770 | 1761, 1774 | 1758, 1772 |
| $\text{Cl}_2\text{C—CO—CCl}_2$ | 1784 | 1750, 1778 | 1745, 1757, 1779 | 1751, 1780 | 1751, 1780 |
| $\text{CH}_3\text{—CO—C(CH}_3)_2$ | 1726 | 1711 | 1705 | 1711 | 1704 |
| $\text{CH}_2\text{Cl—CO—C(CH}_3)_2$ | 1733 | 1712, 1726 | 1717 | 1713, 1732 | 1709, 1725 |
| $\text{CHCl}_2\text{—CO—C(CH}_3)_2$ | 1750 | 1731, 1743 | 1730 | 1731, 1745 | 1729, 1742 |

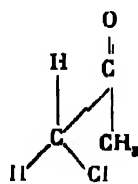
* Shoulder.

In an older interpretation [99] of the doublet occurring in the liquid state, the higher frequency band (1745 cm^{-1}) was assigned to conformation (397) (*anti*) and the lower frequency band (1725 cm^{-1}), to the more polar conformation (396). This interpretation has been revised on the basis of dipole moment measurements and band intensity variations with temperature and dielectric constant of the solvent [98]. In the new interpretation the ν CO frequency at 1715 cm^{-1} (liquid) corresponds to conformation (396) and the lower frequency (1725 cm^{-1}), close to that of acetone, to conformation (397) (*anti*). This conformation is also favored in the vapor phase, absorbing at 1743 cm^{-1} . This interpretation is supported by the increase in intensity of the high frequency band in solvents of high dielectric constant favoring polar structures [98]. However, at higher temperatures the 1725 cm^{-1} band belonging to conformation (397) is stronger. Assignments for the other compounds in Table II-154 were based on the same criteria.

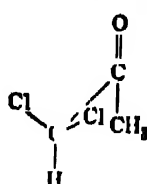
The influence of the size of substituent R^1 in structure (392) on the stability of the conformational isomers can be seen by comparing the spectrum of pinacone with spectra of its halo derivatives. In the vapor phase monochloropinacone has conformation (393) (the ν CO frequency being the same as in pinacone). In the liquid phase or in solution, the predominant form is the more polar conformation (392) with the chlorine and oxygen atoms *cis*. Consequently, in the vapor phase the predominant effect is electrostatic repulsion. In solution steric repulsion also becomes important.



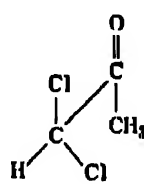
(396)



(397)



(398)



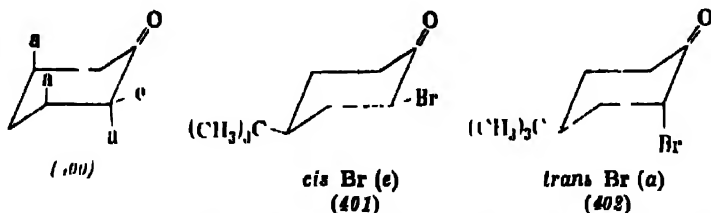
(399)

In dichloroacetone, however, the more stable form in the vapor phase is the more polar one. It is assumed that in this case the more polar form exists in conformation (398) rather than (399).

3. α -Halogenated cyclanones

Spectra of α -halogenated cyclic ketones are particularly interesting with regard to the geometry of these molecules, especially in establishing the configuration of the halogen atom in the α -position.

In α -halogenocyclohexanone, due to the trigonal symmetry of the carbonyl group, an equatorial halogen atom is practically eclipsed by the C=O group, whereas an axial halogen atom is in a staggered position relative to oxygen (400). In conformations with an equatorial halogen atom, the almost parallel dipole of the C-Hal and C=O bonds results in a rise in ν C=O frequency by ca. 20 cm^{-1} . Whereas in a conformation with an axial halogen atom, the orientation of the dipole is such that the carbonyl frequency remains equal to that of the nonhalogenated compound [96, 100]. This fact has been widely used in establishing the configuration of the halogen atom in the α -position in cyclohexanones; for example, in the two isomeric *cis* and *trans*-2-bromo-4-*t*-butylcyclohexanones, the *t*-butyl group is in an equatorial position. In the *cis* isomer (401), the bromine atom is equatorial, and in the *trans* isomer (402) it is axial. The ν CO frequency in the *cis* isomer is shifted by 15–22 cm^{-1} , cf. *t*-butylcyclohexanone (the $\Delta\nu$ variation within these limits is because of a solvent effect). In the *trans* isomer (402), $\Delta\nu$ is practically zero [96, 101, 102].

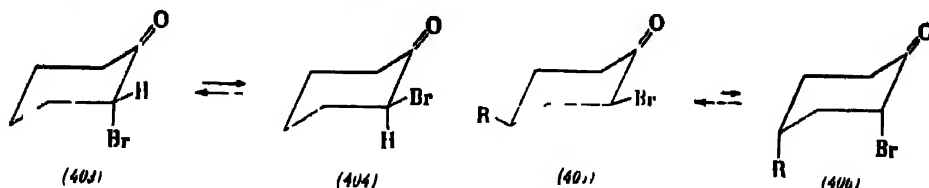


In α -chloro compounds, isomers with equatorial chlorine atoms show $\Delta\nu$ CO shifts of ca. +14 cm^{-1} . Whereas in isomers with axial chlorine atoms these shifts are 2–4 cm^{-1} at the most [103–107].

Of the two conformations possible in α -bromocyclohexanone, (403) with an axial bromine and (404) with an equatorial bromine, conformation (403) predominates: $\Delta\nu$ CO = +1 cm^{-1} [103, 107–110]. This shows that electrostatic repulsion between the carbonyl group and the equatorial bromine atom, corresponding to the *syn* conformation (392) in the acyclic series is larger than steric repulsion between the axial halogen and the two axial hydrogen atoms. However, if the 3-position relative to the bromine atom is substituted with methyl or ethyl groups instead of hydrogen, steric repulsion predominates, and the equilibrium is shifted towards conformation (405) with an equatorial halogen. In 4-methyl- or 1-ethyl-2-bromocyclohexanone, $\Delta\nu$ CO

is 10 cm^{-1} . In 2-bromo-4,4-dimethylcyclohexanone, the halogen atom is exclusively equatorial [103].

In 2,6-dichlorocyclohexanone, the ν_{CO} frequency is 1745 cm^{-1} ($\Delta\nu=33\text{ cm}^{-1}$). The spectrum corresponds to a mixture of 58% *trans* (*a*, *e*) and 42% *cis* (*e*, *e*) or (*a*, *a*). In 2,6-dibromocyclohexanone the ratio is 85% *trans* isomer (*a*, *e*) and 15% *cis* isomer [103].



In α -halogenocycloheptanones the shift, cf. cycloheptanone (1700 cm^{-1}), is $+8\text{ cm}^{-1}$ for the α -bromocompound and $+10\text{ cm}^{-1}$ for the α -chloro derivative [103].

In the case of α -halogenocyclopentanone as a result of the nonplanar half-chair conformation (C_2 symmetry), the angle between the vectors of the dipole moments of $\text{C}=\text{O}$ and $\text{C}-\text{Hal}$ bonds decreases to ca. 77° for both conformations [111]. $\Delta\nu_{\text{CO}}$ in α -bromocyclopentanone is 16 cm^{-1} for the *pseudo*-equatorial bromine atom and 8 cm^{-1} for the *pseudo*-axial bromine atom (intermediate between values corresponding to axial and equatorial halogen atoms in cyclohexanones) [112, 113].

In α -halogenocyclobutanones, frequencies are higher by ca. 25 cm^{-1} cf. 1775 cm^{-1} , the ν_{CO} frequency in liquid cyclobutanone [56]. The frequencies vary with the nature of the solvent. ν_{CO} frequencies of some α -halogenocyclobutanones in various solvents are shown in Table II-155 (concentration $5-10\%$) [56].

Table II-156 shows $\Delta\nu_{\text{CO}}$ values of α -halogenocyclobutanones (Table II-155) in various solvents.

It can be seen that in nonpolar solvents (cyclohexane, isooctane) the ν_{CO} frequency of α -bromocyclobutanone does not vary very much ($\Delta\nu$ is 13 and

15 cm^{-1} , respectively). In more dilute solutions, shifts are even smaller (3 cm^{-1}). However, in polar solvents the effect is appreciable. The frequency rises by $20-25\text{ cm}^{-1}$. This shows that the conformation of the molecule changes with solvent. The geometric model of cyclobutanone (Fig. II-88) corresponds to interconvertible nonplanar forms (407) and (408) [56].

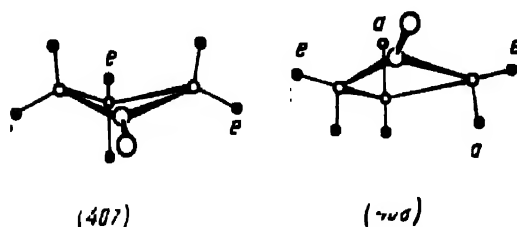


Fig. II-88 Conformations of cyclobutanone.

The molecule has two types of $\text{C}-\text{H}$ bonds, *pseudo*-axial, (*a*) almost perpendicular to the plane formed by the other three carbon atoms, and *pseudo*-equatorial (*e*) lying almost in that plane. On interconversion (407) \rightleftharpoons (408),

Table II-155 ν_{CO} frequencies (cm^{-1}) in α -halogenocyclobutanones in various solvents and in the liquid state


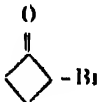
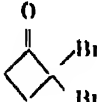
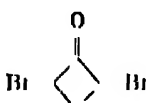
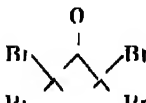
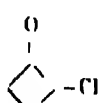
| Formula \ Solvent | Cyclohexane | Isooctane | CCl_4 | Dioxane | CHCl_3 | CH_3OH | $(\text{CH}_3)_2\text{SO}$ | Liquid |
|---|-------------|-----------|----------------|---------|-----------------|------------------------|----------------------------|--------|
|  | 1800 | 1790 | 1789 | 1787 | 1779 | 1780 | 1776 | 1773 |
|  | 1813 | 1814 | 1810 | 1805 | 1801 | 1800 | 1797 | 1795 |
|  | 1814 | 1813 | 1811 | 1805 | 1801 | | 1800 | 1802 |
|  | 1811 | 1810 | 1807 | 1803 | 1805 | | 1798 | 1802 |
|  | 1821 | 1826 | 1823 | 1819 | 1822 | — | 1811 | 1815 |
|  | 1809 | 1810 | 1808 | 1802 | 1801 | | 1796 | 1800 |

Table II-156 Effect of halogens in α -position on $\nu(\text{C}=\text{O})$ frequencies ($\Delta\nu$ of cyclobutanone) [56, 113]

| Solvent | Cyclobutanone | | | | |
|----------------------|---------------|-----------|-------------|-------------|--------------------|
| | 2-Bromo | 2-Chloro, | 2,2-Dibromo | 2,4-Dibromo | 2,2,4,4-Tetrabromo |
| Cyclohexane | 13 | 9 | 14 | 11 | 24 |
| Isooctane | 15 | 11 | 15 | 11 | 27 |
| Dioxane | 18 | 15 | 18 | 16 | 32 |
| Carbon tetrachloride | 21 | 20 | 22 | 18 | 34 |
| Chloroform | 25 | 22 | 25 | 23 | 38 |
| Methanol | 20 | — | — | — | — |
| Dimethylsulfoxide | 21 | 20 | 24 | 22 | 35 |
| Liquid | 20 | 25 | 27 | 27 | 40 |

the *pseudo*-equatorial bonds become *pseudo*-axial and vice versa, the same way as in cyclohexane. According to this model, the halogen atom in the α -position can be either *pseudo*-equatorial (*e*) or *pseudo*-axial (*a*). For reasons discussed in the case of halogenocyclohexanones [111] it is assumed that in polar solvents (where $\Delta\nu \approx 20 \text{ cm}^{-1}$), the favored conformation is that with a *pseudo*-equatorial bromine. Whereas in nonpolar solvents ($\Delta\nu \approx 3 \dots 15 \text{ cm}^{-1}$), the favored conformation is that with a *pseudo*-axial bromine. However, it should be pointed out that electrostatic repulsion also contributes to the rise in νCO frequency, mainly in the *pseudo*-equatorial conformation. In 2-chlorocyclobutanone, the equilibrium is displaced in the same way as in the bromide.

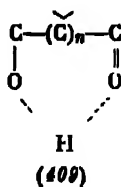
Values in 2, 2-dibromocyclobutanones are close to those in monobromocyclobutanones. Consequently, the bromine atoms are *a* and *e*. In 2, 4-dibromocyclobutanone, shifts are of the same order of magnitude, which implies a structure with one *pseudo*-equatorial and one *pseudo*-axial bromine. The total effect is equal to that of a single bromine atom. The two bromine atoms are *trans*. In 2, 2, 4, 4-tetrabromocyclobutanone, the mean shift of $+31 \text{ cm}^{-1}$ (in CCl_4) corresponds to shifts observed in other tetrabromocyclobutanones ($+36 \text{ cm}^{-1}$) [114].

4. Hydroxyaldehydes and hydroxyketones

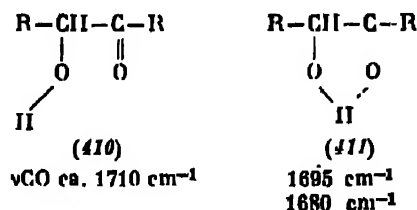
In hydroxyaldehydes and hydroxyketones with functional groups sufficiently removed from each other to prevent intramolecular interaction, the vibrations of $\text{C}-\text{O}-\text{H}$ and $\text{C}-\text{O}$ bonds are similar to those in corresponding monofunctional derivatives. However, in compounds with adjacent OH and $\text{C}=\text{O}$ groups, intramolecular hydrogen bonds are formed, $\text{O}-\text{H} \cdots \text{O}=\text{C} <$, resulting in a number of characteristic absorptions in the infrared [115, 116].

In saturated hydroxyketones the intramolecular hydrogen bonds give rise to a strong absorption in the range $3200-3400 \text{ cm}^{-1}$. On dilution the band corresponding to the free hydroxyl also becomes visible. In the same region the sufficiently strong first overtone of the νCO vibration occurs complicating the interpretation of the spectrum. In such cases deuteration is of great value.

Intramolecular hydrogen bonds in saturated compounds (409) are weak. In α,β -unsaturated keto alcohols, chelation results in a shift of the νOH frequency. The stronger the intramolecular bond, the larger the shift. The infrared spectrum shows a broad band between 2500 and 3200 cm^{-1} . The complexity of this band diminishes its diagnostic value, and study of absorptions in the νCO region becomes necessary [115, 117, 118].



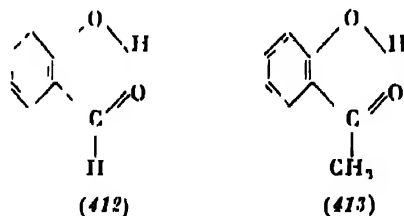
ν CO vibration. The $O-H \cdots O=C$ hydrogen bond diminishes the $C=O$ bond order. The immediate results in a decrease in ν CO frequency. The infrared spectrum of saturated hydroxyketones shows, in addition to the normal strong absorption of the carbonyl group, a new band shifted by $10-15\text{ cm}^{-1}$ toward lower frequencies. This band persists in dilute solutions [117, 118].



The intramolecular hydrogen bond in unsaturated hydroxyaldehydes and hydroxyketones is stabilized by a type of chelate conjugation, and the frequency decreases appreciably (see β -dicarbonyl compounds).

In aromatic hydroxyaldehydes and hydroxyketones, the strength of the intramolecular hydrogen bond can be evaluated from $\Delta\nu$ CO values [119, 119a]. In salicylic aldehyde, the ν CO frequency (1670 cm^{-1}) is shifted by 38 cm^{-1} toward lower frequencies, cf. benzaldehyde (1708 cm^{-1}). This indicates an appreciable diminution of the $C=O$ bonds order in structures such as (412). In *o*-hydroxyacetophenone (413) (ν CO= 1648 cm^{-1}), the shift is 45 cm^{-1} , cf. acetophenone (1693 cm^{-1}).

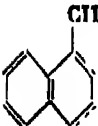
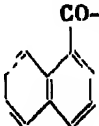
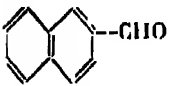
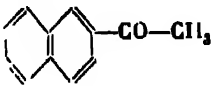
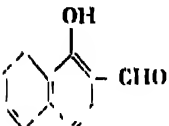
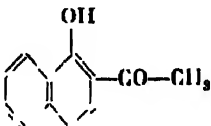
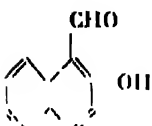
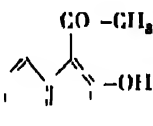
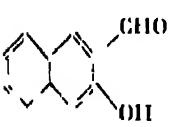
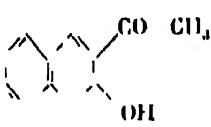
In α - and β -hydroxynaphthaldehyde, shifts in frequency ($\Delta\nu$ CO) vary with the position of CHO and OH groups in the ring [119] (Table II-157).



The table shows that whereas frequencies of functional groups are independent of α or β substitution in the naphthalene ring, in hydroxy derivatives large differences in behavior between the 1, 2- and 2, 3-positions are observed. All compounds form intramolecular (chelate) hydrogen bonds, but they are stronger in compounds substituted in the 1- and 2-position than in those substituted in the 2- and 3-position. The interpretation is that the C_1-C_2 bond in naphthalene has more double bond character than the C_2-C_3 bond and thus stabilizes the chelate bond by conjugation.

Studies of a large number of hydroxy aldehydes and hydroxy ketones in the phenanthrene [120] and indane series [120a] have shown that the decrease in frequency ($\Delta\nu$ CO, cm^{-1}) is 'proportional to the double bond character of the linkage between the substituted carbon atoms.

Table II-157 νCO frequencies in hydroxyl aldehydes and hydroxy ketones in the naphthalene series [119]

| Compound | νCO cm^{-1} | $\Delta\nu\text{CO}$ cm^{-1} | Compound | νCO cm^{-1} | $\Delta\nu\text{CO}$ cm^{-1} |
|---|------------------------------------|--|---|------------------------------------|--|
|  | 1700 | |  | 1695 | — |
|  | 1702 | — |  | 1695 | — |
|  | 1651 | 50 |  | 1625 | 60 |
|  | 1649 | 52 |  | 1625 | 60 |
|  | 1670 | 31 |  | 1675 | 28 |

That angular chelatzation (*414a*, *415a*) is favored over linear chelatzation (*414b*, *415b*) results from comparisons between νCO frequencies in 2, 1-diacetyl- and 4, 6-diacetylresorcinols (*415a* and *415b*).

The lower νCO frequency in compound (*415a*) (stronger hydrogen bond) shows that its conjugated system is more extended than in (*415b*) and that the double bond character between the substituted carbon atoms is stronger. A similar behavior is observed in diacetoxyfloroglucinols [121].

In hydroxyquinones intramolecular hydrogen bonds are possible only with hydroxyl groups in the α -position [122, 117] (Table II-158).

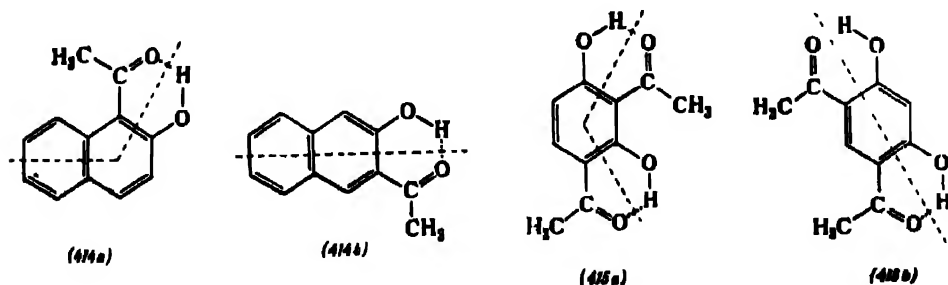
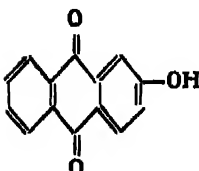
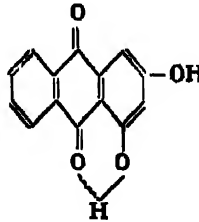
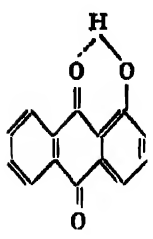
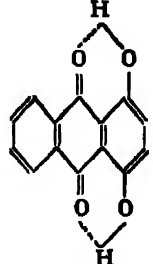


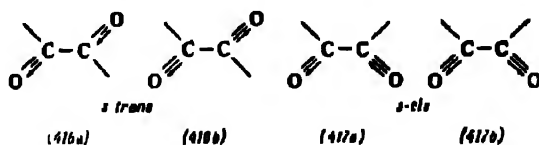
Table II-158 CO and OH frequencies, cm^{-1} , in hydroxy anthraquinones (solid phase)

| Compound | νCO | | νOH | Compound | νCO | | νOH |
|--|----------------|--------|----------------|---|----------------|--------|----------------|
| | free | bonded | bonded | | free | bonded | bonded |
|  | 1673 | — | 3320 |  | 1675 | 1635 | 3380 |
|  | 1673 | 1636 | — |  | — | 1627 | — |

The OH group involved in chelation gives rise to broad absorptions between 2500 and 3200 cm^{-1} .

D. DICARBONYL COMPOUNDS

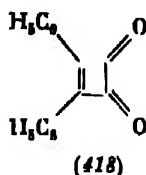
a. **1,2-Dicarbonyl compounds.** In open-chain compounds where the two $-\text{CO}-\text{CO}-$ groups can adopt an *s-trans* orientation only the asymmetric stretching vibration (416a) is active in the infrared. The symmetric vibration (416b) inactive in *trans* configurations becomes active in dicarbonyl compounds where for steric reasons the molecule adopts an *s-cis* configuration (417a) and (417b) (e. g. in cyclic compounds).



Glyoxal $\text{O}=\text{HC}-\text{CH}=\text{O}$ shows a single band at 1730 cm^{-1} , arising from the asymmetric stretching vibration of the two *trans* oriented $\text{C}=\text{O}$ groups [123, 124]. The shift toward higher frequencies, cf. saturated aldehydes, is negligible (ca. 5 cm^{-1}). This shows that the two groups are not conjugated.

Diketones with carbonyl groups in the 1- and 2-positions show the same behavior. Spectra show a single absorption shifted by ca. +5 cm^{-1} , cf. the corresponding monoketones; for example, diacetyl absorbs at 1718 cm^{-1} , alipha-

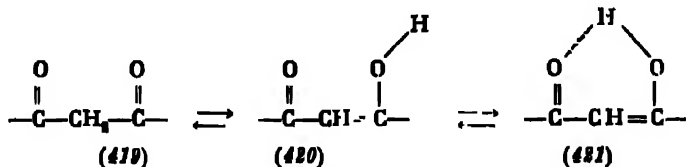
tic monoketones absorb at 1715 cm^{-1} , and benzyl absorbs at 1681 cm^{-1} (in the region of aromatic monoketones) [124]. The spectrum of pyruvic aldehyde $\text{CH}_3\text{—CO—CHO}$ shows a broader band centered around 1721 cm^{-1} , containing the absorptions of both types of carbonyl groups [125]. Cyclic six-membered ring 1,2-diketones (*s-cis* configuration) absorb at 1730 and 1760 cm^{-1} and five-membered ring ketones absorb at 1760 and 1775 cm^{-1} [126]. If the two groups belong to a four-membered ring the frequency is higher; for example, diphenylcyclobutenedione (418) has a doublet at 1776 and 1786 cm^{-1} [127].



b. **1,3-Dicarbonyl compounds.** Spectra of 1,3-dicarbonyl compounds reflect their special properties. In general, the so-called "pure" substances are not individual compounds, but tautomeric equilibria of keto-enol forms. Because of this, normally the infrared spectrum shows characteristic bands for the molecular species present. The tautomeric equilibrium ketone \rightleftharpoons enol depends on solvent, dilution, and temperature. Consequently, studies of intensity variation are of special value in the investigation of these compounds.

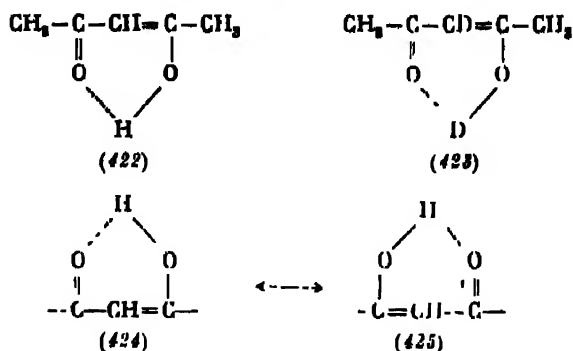
Infrared spectroscopy is particularly efficient in the investigation of this type of tautomerism.

In the case of β -diketones, the spectrum should show three types of bands in the carbonyl region: saturated ketone (419), α , β -unsaturated ketone (420), and bonded carbonyl (421).

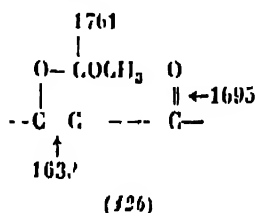


The spectrum of acetylacetone in the liquid state [124, 128] shows in the carbonyl region a doublet of medium intensity ($1709\text{--}1729\text{ cm}^{-1}$) assigned to the ketonic form (the splitting is attributable to vibrational coupling). The enolic form shows only a broad, very strong band between 1538 and 1640 cm^{-1} . The band includes the absorptions of both functional groups, $\text{C}=\text{C}$ and $\text{C}=\text{O}$ modified by hydrogen bonding. This absorption corresponds to a chelate structure (421) resulting from an intramolecular hydrogen bonding between the carbonyl group (acceptor) and the enolic hydroxyl group (donor). The νCO frequency in the enolic form (422) (1616 cm^{-1}) was established by deuteration. In the deuteroderivative (423) it occurs at 1621 cm^{-1} . The $\nu\text{C}=\text{C}$ vibration in (422) has a frequency of 1536 cm^{-1} [129]. The band arising from the chelate linkage persists on dilution as in intramolecular hydrogen bonding

in hydroxylic compounds. For chelate structures a stabilization due to resonance between structures (424) and (425) is assumed.

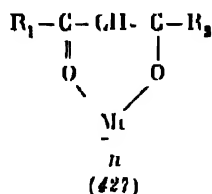


On acetylation of the OH group (in the enolic form) the possibility of chelation disappears. The spectrum of the acetyl derivative (426) shows the normal bands of an α, β -unsaturated carbonyl (1695 cm^{-1}), of the $\text{C}=\text{C}$ bond (1633 cm^{-1}), and of the $\text{C}-\text{O}$ linkage in the acetyl group (1761 cm^{-1}).



Liquid acetylacetone shows in the $\nu(\text{OH})$ vibration region a broad band within the range $2500-3600 \text{ cm}^{-1}$, assigned to the bonded enolic form. A second broad band, at 2700 cm^{-1} , occurring in solution and in the vapor phase is assigned to the chelate $\text{O}-\text{H}$ bond [129]. Bands in this region are characteristic for intramolecularly bonded hydroxyketones.

In metal chelates of the type (427)



the chelate $\text{O}-\text{H}$ frequency at 2700 cm^{-1} does not occur. $\nu\text{C}=\text{O}$ absorptions fall within the range $1600-1616 \text{ cm}^{-1}$ and $\nu\text{C}=\text{C}$ frequencies arise between $1502-1518 \text{ cm}^{-1}$ comparable with chelated phenol [129].

In cyclic 1,3-diketones, no resonance stabilized intramolecular chelate bond can be formed. The enolic structure enables dimerization and polymerization by means of intermolecular hydrogen bonds.

The spectrum of dimethyldihydroresorcinol shows bands corresponding to these forms [121, 128]. In chloroform solution the two tautomeric forms are in equilibrium (Fig. II-89). The keto form (428) absorbs at 1735 and 1708 cm^{-1} and the dimeric enol form (430) absorbs at 1607 cm^{-1} .

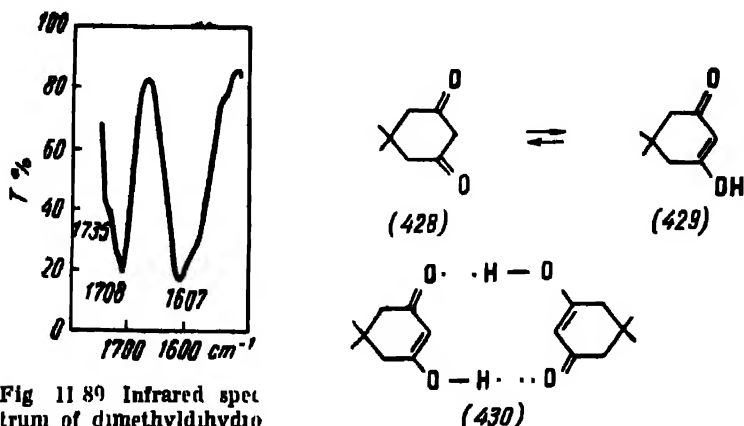


Fig II 89 Infrared spectrum of dimethyldihydroresorcinol in chloroform solution.

On increasing the concentration the equilibrium shifts toward the enolic form (dimer or polymer). The intensity of the 1607 cm^{-1} band rises. Bulky

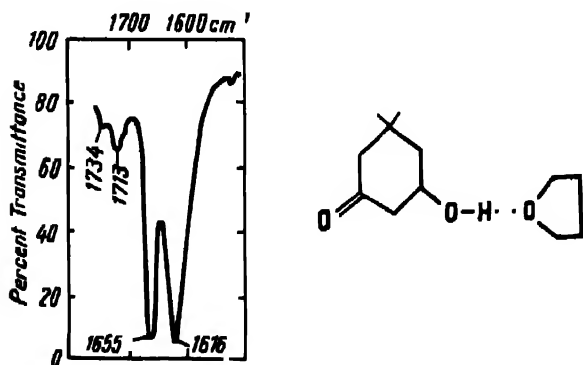


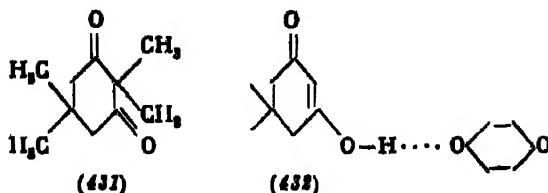
Fig II 90 Infrared spectrum of dimethyldihydroresorcinol in the presence of tetrahydrofuran

are also formed. The spectrum shows a single band at 1607 cm^{-1} as in the dimer of the enol (430).

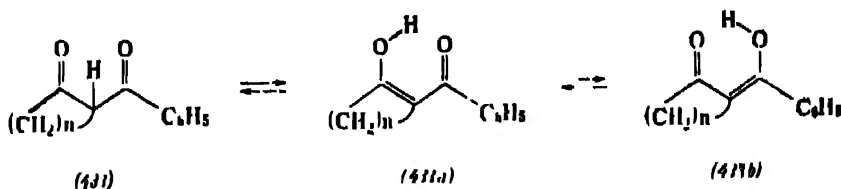
When ethers are used as solvents (e.g. dioxane), the OH group of the enol form (432) associates with the solvent. The spectrum shows weak bands arising from the keto-form at 1711 and 1713 cm^{-1} , along with strong bands of the solvated enol, at 1655, 1616 cm^{-1} [128] (Fig. II-90).

substituents in the 2-position diminish the intensity of the band characteristic for the enol form; consequently they shift the equilibrium toward the keto form. The assignment of the carbonyl band is supported by the pattern of the spectrum of tetramethyleyclohexane 1,3-dione (431) which exists only in the keto form (absorptions at 1688 and 1717 cm^{-1}).

In alcoholic solution, hydrogen bonds with solvent



In a number of 2-benzoylcyclanones with five-, six- and seven-membered rings [general formula (433)], the νCO band in the cycloalkane ring occurs along with the νCO band of the aromatic carbonyl group ($\text{C}_6\text{H}_5-\text{CO}-\text{R}$).



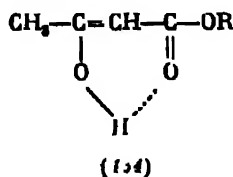
The carbonyl frequency of the enolic form, involved in the chelate bond lies in the range $1510\text{--}1610\text{ cm}^{-1}$ (Table II-159).

Table II-159 νCO frequencies in β -diketones (2-benzoylcyclanones)

| 2-Benzoyl | No. of ring carbons | $\nu\text{CO}, \text{cm}^{-1}$ | | Enol frequency, cm^{-1} | Amount of enol, % |
|----------------|---------------------|--------------------------------|-------------------------------------|----------------------------------|-------------------|
| | | cyclo-alkane | conjugated ($\alpha\text{-aryl}$) | | |
| Cyclopentanone | 5 | 1743 <i>m</i> | 1690 <i>s</i> | 1510–1610 <i>s</i> | 39 |
| Cyclohexanone | 6 | 1724 <i>s</i> | 1683 <i>s</i> | 1589–1603 <i>w</i> | 3 |
| Cycloheptanone | 7 | 1720 <i>w</i> | 1688 <i>w</i> | 1520–1620 <i>s</i> | 9 |
| Indanone | 5 | — | — | 1500–1640 <i>s</i> | 78 |
| Tetralone | 6 | — | — | 1480–1610 <i>s</i> | 25 |
| Benzosuberone | 7 | — | — | 1500–1620 <i>s</i> | 48 |

Variations in band intensities (in 1% solutions) enabled the determination of the amount of enol in five-membered (39%), six-membered (3%), and seven-membered (9%) cyclic compounds [130].

It has been observed that in benzoylcyclanones, where the $\text{C}=\text{O}$ group of the cycloalkane ring is conjugated with the aromatic ring, the tendency toward enolization is much greater (compare indanone with tetralone and benzosuberone in Table II-159). The νOH region does not show the free OH band, which indicates total chelation.



c. **Keto-enolic tautomerism.** The tautomerism of β -ketoesters is similar to that described above. Acetoacetic ester $\text{CH}_3\text{COCH}_2\text{COOR}$ (434), where $\text{R}=\text{CH}_3$ shows two bands (1743 and 1723 cm^{-1}) in the νCO region, corresponding to absorptions of the $\text{C}=\text{O}$ group in COOCH_3 and of the keto group in β -position, [128]. The ethyl ester ($\text{R}=\text{C}_2\text{H}_5$) absorbs at 1738 and 1717 cm^{-1} . The small amount of chelated enol (3%) gives rise to a νCO absorption at 1668 cm^{-1} . The $\nu\text{C}=\text{C}$ band occurs at 1640 cm^{-1} .

The size of the α -substituent has an influence on the tautomeric equilibrium. In a number of α -substituted acetoacetic esters with substituents ranging from methyl to *t*-butyl and rings from 3–6 atoms, the tautomeric equilibrium has been determined on the basis of infrared spectra. It must be pointed out that cyclobutylacetoacetic ester exists exclusively in the keto-form (νCO at 1725 cm^{-1}) [131, 132].

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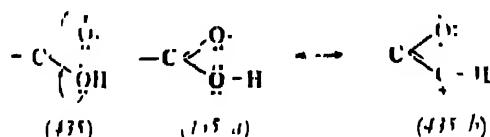
CHAPTER 7

CARBOXYLIC ACIDS

Organic acids RCOOH are characterized by the vibrations of the carboxylic group. In general the hydrocarbon group R shows normal frequencies. Interactions between the R group and the COOH group is limited to the COOH group and the atoms in its immediate vicinity.

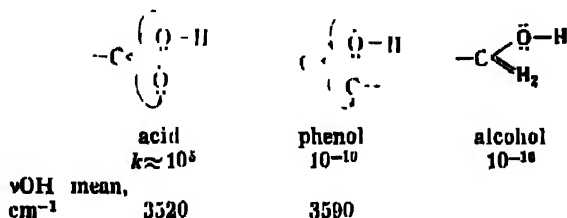
The carboxyl group can be considered as being formed from C=O and OH units, characteristic for carbonyl and hydroxyl compounds, respectively. Although these units can be identified separately in the infrared spectrum, because of conjugation between the two oxygen atoms, fundamental changes in the nature of C=O and C-O-H bonds take place. As a consequence new, characteristic properties of the functional group occur, both from the chemical as well as vibrational point of view.

The internal conjugation of the carboxyl group (435, 435a, 435b) results in decreased C=O and O-H bond orders leading to a lower force constant, hence lower frequency of these vibrations.



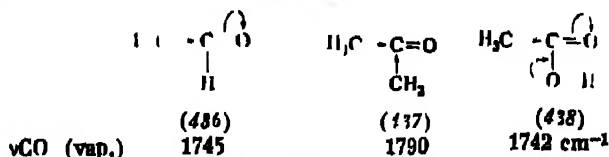
The influence of internal conjugation of the carboxyl group on properties of the O-H bond can be seen by comparing νOH frequencies and acidity constants in acids, phenols, and saturated alcohols [1].

The decrease in νOH frequency in acids, cf. alcohols, exceeds 100 cm^{-1} . In phenols, with a much weaker conjugation, both the acidity constant and the νOH frequency have intermediate values. It has been shown that a linear relationship exists between the νOH frequency and the acidity constant pK_a [2].

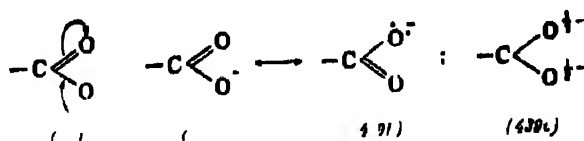


The C=O frequency in the carboxyl group is ca. $40\text{--}50\text{ cm}^{-1}$ higher than in aldehydes and ketones [compare (436)–(438)]. It could be expected that substitution of the hydrogen atom in an aldehyde with the electronegative oxygen atom ($-I$ effect) would result in a larger rise in frequency (in the extreme case of acid fluorides $\text{CH}_3\text{--COF}$, where only a strong $-I$ effect is at work,

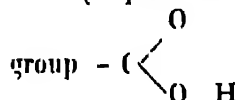
the frequency rises to 1872 cm^{-1} , i.e. by 127 cm^{-1} . The relatively low rise in frequency is due to conjugation acting in this case in the opposite direction to the inductive effect. It is clear, however, that the $-I$ effect has a larger contribution. α , β -Unsaturated aldehydes, where the conjugative effect is stronger than the $-I$ effect of the $\text{C}=\text{C}$ bonds, have lower $\nu\text{C}=\text{O}$ frequencies than the saturated analogs.



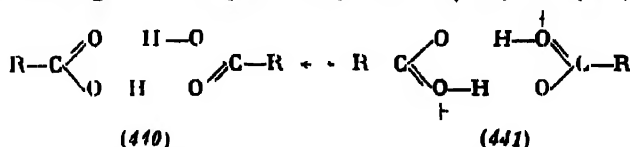
In the carboxylate ion (439), the prevalent conjugation (439a) and (439b) makes the two $\text{C}-\text{O}$ bond orders equal (439c). The group behaves as a unit and the frequency decreases to $1550-1600\text{ cm}^{-1}$.



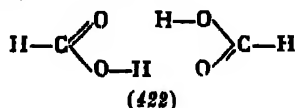
The carboxyl group has six vibration modes three stretching vibrations of $\text{O}-\text{H}$, $\text{C}=\text{O}$, and $\text{C}-\text{O}$ bonds, two deformation vibrations of the $\text{O}-\text{H}$ bond (in-plane and out-of-plane), and a deformation vibration of the whole



As a result of its special structure, the carboxyl group has a strong tendency toward hydrogen bonding, forming dimers (440) and (441)



The formation of these bridges lowers the force constant, and the frequency of $\text{C}=\text{O}$ and $\text{O}-\text{H}$ bonds. The large decrease in frequency in these dimers reflects the exceptional strength of hydrogen bonds formed by the association of carboxyl groups. This is attributable to the stabilization of cyclic dimers, by a resonance of type (440) and (441) [1, 3]. For example, the dimer of formic acid (442) has a C_{2v} symmetry [1]. The decrease in νCO frequency in structure (440) is ca. 50 cm^{-1}

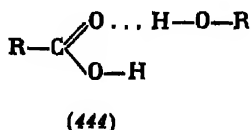
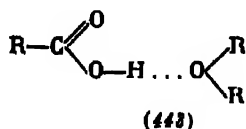


The bonded νOH vibration gives rise to a broad band covering the range $2500-3000\text{ cm}^{-1}$. Other forms of association of the carboxyl group also con-

tribute to this band. In the crystalline state, liquid state, or concentrated solutions, carboxylic acids exist almost exclusively as dimers. The monomeric carboxyl can be identified only in very dilute solutions (less than 0.01 M in nonpolar solvents) or in the vapor phase. Since most experimental work has been performed under conditions in which acids are dimerized, the current frequencies correspond to this structure.

Acids form hydrogen bonds with polar solvents [4a, 4b], but they are incomparably weaker than those formed between two carboxyl groups: consequently, shifts are smaller. Frequencies are intermediate between monomeric and dimeric carboxyl groups.

Depending on the nature of the solvent, the carboxyl group can form hydrogen bridges either by the intermediacy of the carbonyl oxygen, or the hydroxyl oxygen. For example, in solutions of ethers (ethyl ether, dioxane, tetrahydrofuran), the bonded molecule has structure (443) and the mean frequency decreases to 1735 cm^{-1} . In alcohols the other oxygen atom is involved (as proton acceptor) (444) and the νCO frequency decreases to 1720 cm^{-1} .



In nonpolar solvents the mean frequency is 1760 cm^{-1} , and in the vapor phase it is 1780 cm^{-1} . Dimer (440) has a frequency of 1730 cm^{-1} in the vapor phase and 1710 cm^{-1} in a nonpolar solvent [5].

Shifts in carboxyl frequencies as a result of electronic (inductive and conjugative) effects and of possible interactions between the carboxyl group and various polar substituents in the molecule enable the differentiation between various classes of organic acids.

A. SATURATED CARBOXYLIC ACIDS

a. Vibrations of the COOH group

a. νOH stretching vibration. The νOH frequency in the free (monomeric) carboxyl can be identified in spectra of acids in the vapor phase at high temperature or in dilute solution (below 0.01 M) in nonpolar solvents [6, 7]. A band around $3500\text{--}3570\text{ cm}^{-1}$ was assigned to this vibration [7]. Formic acid in the vapor phase absorbs at 3570 cm^{-1} and acetic acid, at 3545 cm^{-1} [8]. In most cases the bonded form (dimer) also persists under these conditions. Consequently, the νOH band arising from the free carboxyl usually occurs along with the broad band of the bonded carboxyl ($2500\text{--}3000\text{ cm}^{-1}$).

Table II-160 shows $\nu\text{C}=\text{O}$, νOH , and νOD frequencies of monomeric acetic acid (vapor phase), of its dimer, and of deuterated acids [8].

The νOH frequency in the free carboxyl is lower in solution than in vapor phase. The difference can be as large as 50 cm^{-1} .

Table II-160 ν_{OH} and $\nu_{C=O}$ frequencies in acetic and deuterioacetic acids [8]

| Vibration | Monomer | | | | Dimer | | | |
|-------------|------------|------------|------------|------------|------------|------------|------------|------------|
| | CH_3COOH | CH_3COOD | CD_3COOH | CD_3COOD | CH_3COOH | CH_3COOD | CD_3COOH | CD_3COOD |
| $\nu_{C=O}$ | 1770 | 1770 | 1760 | 1760 | 1739 | 1725 | 1730 | 1740 |
| ν_{O-H} | 3546 | — | 3640 | — | 2990 | — | 3106 | — |
| ν_{O-D} | — | 2653 | — | 2660 | — | 2260 | — | 2260 |

In the solid state, liquid state, or concentrated solution, carboxylic acids are associated as dimers (or polymers) [4]. The infrared spectrum does not show the band arising from the monomeric form. It shows the broad band of the bonded carboxyl, between 2500 and 3000 cm^{-1} [6, 7, 9]. Also, superimposition with CH stretching vibrations takes place in this region: consequently, correlations between this band and the structure of the acid are not reliable.

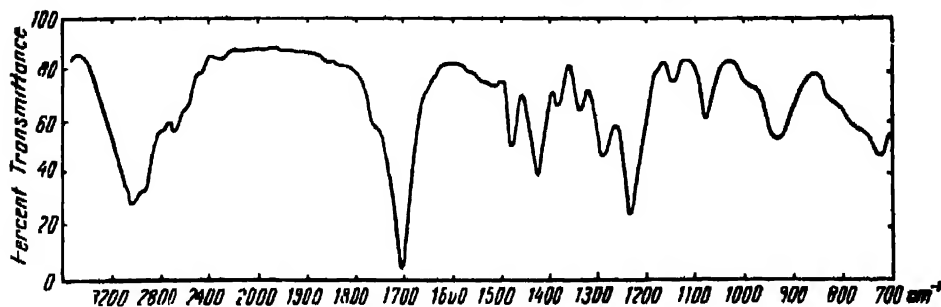


Fig. II-91 Infrared spectrum of propionic acid

However, this band is of great practical value. Since the majority of spectra are recorded in the solid phase, liquid phase, or in solution, this absorption

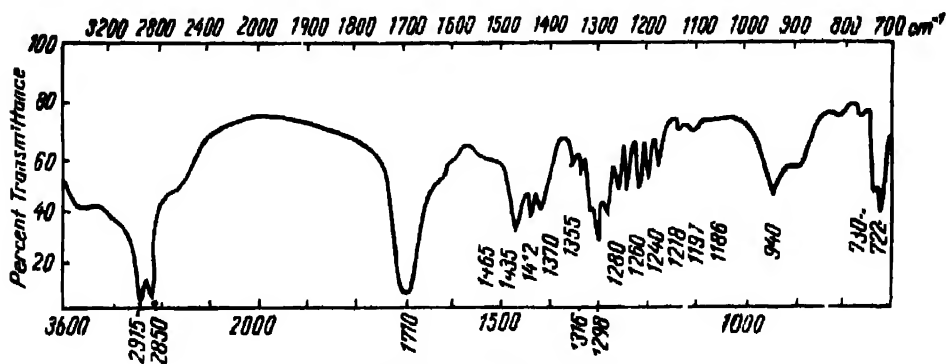


Fig. II-92 Infrared spectrum of stearic acid.

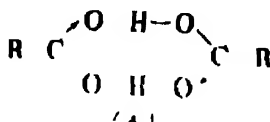
occurs in each spectrum of an acid and serves for the identification of the functional group. Figure II-91 shows the infrared spectrum of propionic acid (solution) and Fig. II-92 that of solid stearic acid.

Two characteristic aspects of the νOH band arising from the bonded carboxyl can be noticed: the considerable shift toward lower frequencies, cf. other bonded OH groups (e.g. alcohols, phenols), and the large number of satellite bands of variable intensity spread over a large region of the spectrum. The interpretation of these bands is discussed in several papers [6, 7].

The reasons for the shifts have been stated previously. The occurrence of satellite bands has been interpreted in various ways by different workers [6, 7]. By analogy with hydrogen bonding in alcohols, it was assumed that the broad band is due to a number of hydrogen bonds of various lengths [10]. In a different interpretation, the band is assigned to a coupling between the fundamental vibration of the OH bond and other lower frequency vibrations of the dimer [11, 12]. Deuteration has shown that satellite bands can be explained satisfactorily as being combination bands of different low-frequency vibrations arising from the carboxyl group intensified by Fermi resonance [13]. The stronger band at 2700 cm^{-1} is assigned to a combination of coupled frequencies C—O and O—H at 1420 and 1300 cm^{-1} . On deuteration the frequencies decrease to 2100 and 1050 cm^{-1} , respectively [13].

Weak bands occur in the $2500 - 2700\text{ cm}^{-1}$ region. Sometimes they are of value in the identification of acids in a homologous series [6, 7]. Chelate compounds of enolic forms of β -keto esters absorb in the same region, but the pattern is completely different [14, 15]. Sulfur compounds have sharp, well defined bands.

b. $\nu\text{C}=\text{O}$ stretching vibration. The vibration of the $\text{C}=\text{O}$ bond in the carboxyl group gives rise to characteristic absorptions both in the case of free and bonded carboxyl. Since majority of spectra of acids are recorded in the solid state, liquid state, or in relatively concentrated solution, the frequencies discussed are those arising from dimers. Assuming for the dimer of formic acid the planar structure (442) with C_{2h} symmetry [4, 8] the presence of a symmetry plane makes only the asymmetric vibration (445) active in the infrared [16, 17]



1. $\nu\text{C}=\text{O}$ frequency (monomer). In saturated aliphatic acids in the vapor phase or in dilute solution (below 0.01 M), a band of mean frequency 1790 cm^{-1} [18] and 1760 cm^{-1} (in CS_2 or CCl_4 , respectively) [9, 16] has been assigned to this vibration. The absorption of the monomeric form of formic acid in the vapor phase occurs at 1794 cm^{-1} [18]. The band intensity ratio monomer / dimer varies with temperature; for example, acetic acid in the vapor phase at 20°C shows two bands: 1735 cm^{-1} , assigned to the dimer and 1785 cm^{-1} , assigned to the monomer. At 60°C the higher frequency band (1794 cm^{-1}) becomes stronger, which shows that at higher temperatures the amount of monomer increases [18, 19]. Similar variations also take place in other acids.

Many carboxylic acids in dilute solutions of nonpolar solvents (CCl_4 , CS_2) show a weak band at ca. 1760 cm^{-1} along with the strong band of the

dimer at $1710 \pm 8 \text{ cm}^{-1}$ [15, 19, 20]. The exact position of the monomeric νCO band depends on the nature of both the acid and the solvent. In polar solvents the frequency decreases due to hydrogen bonding between the carboxyl group and the solvent. In ethereal solutions, for example, in dioxane (Fig. II-93), the frequency is 1735 cm^{-1} , 25 cm^{-1} lower than in nonpolar solvents [5]. In alcohols, the stronger hydrogen bonds $>\text{C}=\text{O} \cdots \text{H}-\text{OR}$ result in a larger frequency shift ($35-40 \text{ cm}^{-1}$) [20, 21].

Intensity variations of the two bands monomer-dimer at different concentrations have been used to determine the equilibrium constant [22, 23].

2. $\nu\text{C}=\text{O}$ frequency (dimer). In the crystalline state, liquid film, or concentrated solution, spectra of carboxylic acids show a single band, that of the dimer.

Saturated monocarboxylic aliphatic acids have a mean frequency of $1710 \pm 10 \text{ cm}^{-1}$ [18-20, 24]. The frequency varies with experimental conditions. In the crystalline state the frequency is $10-26 \text{ cm}^{-1}$ lower than in the liquid state [24, 25]. A different behavior is shown by acetic acid where the decrease in frequency between the liquid and crystalline state is 61 cm^{-1} [25]. Frequencies of some monocarboxylic saturated acids in the liquid and crystalline state are shown in Table II-161.

Table II-161 νCO frequencies in monocarboxylic acids [25]

| Acid | Formula | $\nu\text{CO}, \text{cm}^{-1}$ | | $\Delta\nu$ cm^{-1} | Solution in $\text{CS}_2, \text{CCl}_4$ |
|------------|--|--------------------------------|-------------|---------------------------------|--|
| | | liquid | crystal | | |
| Acetic | CH_3-COOH | 1715 | 1654 | 61 | 1710 ± 10 |
| Propionic | $\text{CH}_3-(\text{CH}_2)-\text{COOH}$ | 1725 | 1730, 1710* | | |
| Butyric | $\text{CH}_3-(\text{CH}_2)_2-\text{COOH}$ | 1729 | 1740, 1705 | | |
| Valeric | $\text{CH}_3-(\text{CH}_2)_3-\text{COOH}$ | 1722 | 1722 | 0 | |
| Capronic | $\text{CH}_3-(\text{CH}_2)_4-\text{COOH}$ | 1721 | 1710 | -11 | |
| Oenanitic | $\text{CH}_3-(\text{CH}_2)_5-\text{COOH}$ | 1724 | 1710 | 14 | |
| Caprolic | $\text{CH}_3-(\text{CH}_2)_6-\text{COOH}$ | 1722 | 1702 | 20 | |
| Nonanoic | $\text{CH}_3-(\text{CH}_2)_7-\text{COOH}$ | 1726 | 1700 | 26 | |
| Caprinic | $\text{CH}_3-(\text{CH}_2)_8-\text{COOH}$ | 1716 | 1705 | 11 | |
| Dodecanoic | $\text{CH}_3-(\text{CH}_2)_{10}-\text{COOH}$ | 1720 | 1705 | 15 | |

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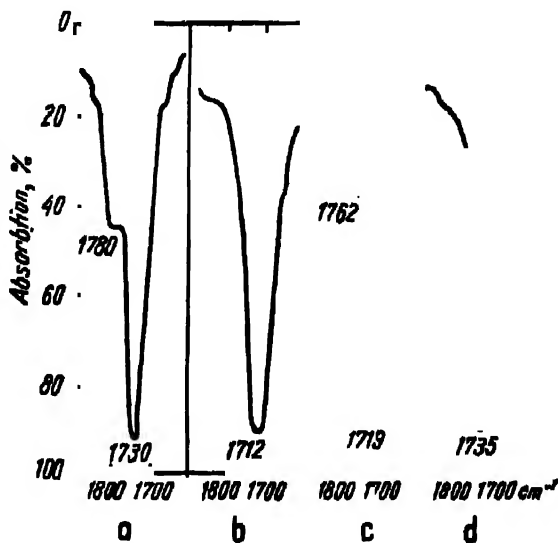


Fig. II-93 Infrared spectrum of propionic acid in the C=O region:

(a) vapor (+30°C); (b) liquid film; (c) 0.5 M solution in CCl_4 , and (d) solution in dioxane.

Stearic acid has the same frequency (1698 cm^{-1}) in the solid state as in liquid film [26].

In higher aliphatic acids with chains containing 14–21 carbon atoms, an alternation of the $\nu\text{C}=\text{O}$ frequency between even- and odd-numbered members has been observed. The even-numbered members (C_{14} , C_{16} , C_{18} , C_{20}) have the highest absorption at $1698\text{--}1701\text{ cm}^{-1}$, whereas in odd-numbered members (C_{17} , C_{19} , C_{21}), it occurs at 1705 cm^{-1} [26]. In lower members no such alternations have been noticed (Table II-161) [25].

Branching in the α -position lowers the $\text{C}=\text{O}$ frequency. Electron releasing methyl groups (+ I-effect) reduce the $\text{C}-\text{O}$ bond order and simultaneously strengthen the $\text{O}-\text{H}$ bond. Decrease in frequency parallels the decrease in dissociation constants of these acids [27, 28]. νCO frequencies and dissociation constants of some α -substituted acetic acids are shown in Table II-162.

Table II-162 νCO frequencies in α -substituted acetic acids [28, 29]

| Acid | $\nu\text{CO}, \text{ cm}^{-1}$ in CCl_4 | $K_a \cdot 10^{-5}$ |
|--|--|---------------------|
| $(\text{CH}_3)_3\text{C}-\text{COOH}$ | 1704 | 0.98 |
| $(\text{CH}_3)_2\text{CH}-\text{COOH}$ | 1715 | 1.40 |
| CH_3-COOH | 1721 | 1.86 |
| ICH_2-COOH | 1721 | 74 |
| $\text{BrCH}_2-\text{COOH}$ | 1730 | 138 |
| $\text{ClCH}_2-\text{COOH}$ | 1736 | 155 |
| $\text{Cl}_2\text{CH}-\text{COOH}$ | 1751 | 5000 |
| $\text{Cl}_3\text{C}-\text{COOH}$ | 1764 | 130000 |

Recordings of acid spectra in mulls of alkaline halides involve some complications because of possible interactions between the carboxyl group and the halide [29, 30].

The integrated intensity of the νCO band in saturated acids varies very little within the series. In general it is smaller in aliphatic than in aromatic acids [30].

3. *Saturated dicarboxylic acids.* In the first two members of the series, interactions between the COOH groups take place. Anhydrous oxalic acid or its dihydrate has a strong absorption between 1690 and 1710 cm^{-1} . Crystalline malonic acid shows a doublet with a strong component at 1710 cm^{-1} and a weaker one at 1740 cm^{-1} . The same pattern is shown by succinic acid, with a strong band at 1700 cm^{-1} and a weak band at 1780 cm^{-1} . The higher members have a single absorption: adipic and suberic acids at 1700 cm^{-1} in nujol [9], 1704 and 1706 cm^{-1} , respectively, in KBr [30]. The other dicarboxylic acids in the homologous series do not show any particularities in the νCO region, cf. monocarboxylic acids.

Attempts to distinguish enantiomeric forms of α -substituted dicarboxylic acids in the infrared failed [7].

c. *Other vibrations of the carboxyl group.* Besides the vibrations discussed, the dimeric carboxylic group ($\text{--COOH}\cdots\text{HOOC--}$) gives rise to bands at 1420 ± 20 ,

1300 ± 15 and 935 ± 15 cm^{-1} [31]. The first two bands were assigned to the coupling of the OH deformation mode with the C—O stretching vibration occurring in the plane of the ring formed by the dimeric carboxyl groups. The third is assigned to the out-of-plane OH deformation mode. A low frequency band (680 cm^{-1}) has been assigned to the deformation vibration of

the angle $\text{C} \begin{array}{c} \text{O} \\ \diagup \\ \text{O}- \end{array}$ [25].

These bands, arising from dimeric forms disappear in dilute solution [31, 32]. In some polymorphic forms their frequencies can be shifted by as much as ~ 50 cm^{-1} . The presence or absence of these bands has been mentioned without any interpretation in numerous works dealing with acids [7, 32].

On deuteration the bands get displaced accordingly to the displacement $\text{O}-\text{H} \rightarrow \text{O-D}$ [28, 31] (Table III-163).

Table II 163 Characteristic frequencies of the carboxyl group between 600 and 1500 cm^{-1}

| Acid | R—COOH | | | R—COOD | | |
|-----------|--------|------|-----|--------|------|-----|
| Acetic | 1412* | 1290 | 935 | 1320 | 1058 | 670 |
| Propionic | 1419* | 1239 | 937 | 1302 | 1043 | — |
| Laurinic | 1432* | 1234 | 934 | 1367 | 1055 | 665 |
| Stearic | 1435 | 1300 | 940 | 1366 | 1058 | 666 |

* The frequencies of these bands are temperature dependent.

Characteristic frequencies of the dimeric carboxyl in dicarboxylic acids are shown in Table II-164 [30].

Table II 164 Characteristic frequencies of COOH and COOD groups in the 900—1570 cm^{-1} region [30]

| Acid | COOH | | | COOD | | |
|----------|-------------------|------|-----|-------|------|-----|
| Oxalic | 1396 | 1224 | 916 | 1228 | 1046 | — |
| Malonic | 1437 ¹ | 1311 | 922 | 1372* | 1046 | 672 |
| Succinic | 1417* | 1314 | 925 | 1363 | 1046 | 680 |
| Glutaric | 1430 | 1305 | 933 | 1332 | 1049 | 675 |
| Adipic | 1431 | 1285 | 937 | 1300 | 1050 | 675 |

* Uncertain

b. *Vibrations of the hydrocarbon radical.* In saturated alkylcarboxylic acids, the influence of the carboxyl group is felt only by the CH_2 group in

the α -position ($-\text{CH}_2-\text{COOH}$). Characteristic frequencies of the rest of the hydrocarbon chain, not influenced by chain length, are shown in Table II-165.

Table II-165 Characteristic frequencies (cm^{-1}) of α, β -unsaturated acids

| Vibration mode | Group | Frequency cm^{-1} |
|---|-----------------------|-------------------------------|
| $\nu\text{CH asym}$ | CH_2 | 2954 |
| $\nu\text{CH asym}$ | CH_2 | 2926 |
| $\nu\text{CH sym}$ | CH_2 | 2872 |
| $\nu\text{CH sym}$ | CH_2 | 2853 |
| CH deformation | CH_2 | 1460 |
| CH deformation | $\alpha \text{ CH}_2$ | 1410 |
| $\text{as. CH}_2 \text{ deformation}$ | CH_2 | 1372 |
| $\gamma\text{CH}_2 \text{r in chains with } n \geq 1$ | | |
| $\text{CH}_2 \text{ groups}$ | CH_2 | 720 |

a. **CH stretching vibrations.** In the C-H stretching vibration regions CH_2 groups give rise to strong absorptions at 2926 ($\nu\text{CH}_2 \text{ asym}$) and 2853 cm^{-1} ($\nu\text{CH}_2 \text{ sym}$). The terminal CH_3 group gives rise to two weaker bands at 2951 cm^{-1} ($\nu\text{CH}_3 \text{ asym}$) and 2872 cm^{-1} ($\nu\text{CH}_3 \text{ sym}$). The behavior of these bands in chains of various lengths parallels that of straight-chain alkanes.

b. **CH deformation vibrations.** The four deformation modes of CH_2 groups (see Alkanes) give rise to absorptions in the same region as in *n*-alkanes [26]. Some particular aspects are mentioned below.

The scissoring vibration of CH_2 groups gives rise to a normal absorption in range 1460–1470 cm^{-1} . Along with this band, a strong band is noticed at 1405–1410 cm^{-1} assigned to the scissoring vibration of the CH_2 group adjacent to the carboxyl [26, 33]. This absorption disappears in γ -substituted acids [34, 35] or in α, β -unsaturated acids. In saturated acids with less than 11 carbon atoms, the absorption at 1410 cm^{-1} is stronger than that at 1470 cm^{-1} . The latter becomes stronger in chains with more than 11 carbon atoms [34].

The in-plane rocking vibration of the CH_2 group ($\gamma\text{CH}_2 \text{r}$) in straight-chain aliphatic acids gives rise to an absorption at 720 cm^{-1} . As in long chain *n*-alkanes, in the solid state the band splits into components [26]. The relative intensity of the band increases with the number of CH_2 groups. The apparent molar extinction coefficient increases from 37 units in myristic acid (C_{14}) by 3 units for each CH_2 group up to C_{21} (heneicosanoic acid).

The band shows dichroism, as in any *n*-alkane chain. In mono- and dicarboxylic acids with 2–12 carbon atoms, this absorption occurs in the range 720–810 cm^{-1} [24, 25, 26] (Table II-166).

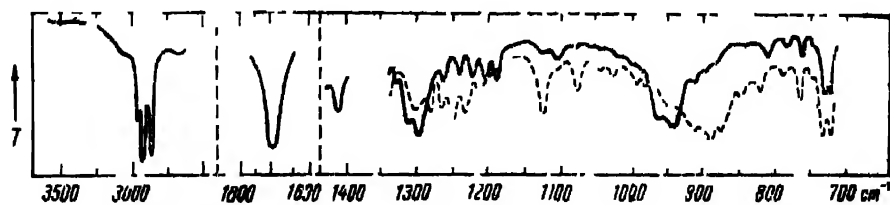
c. **Characterization of individual members of the series.** Spectra of various aliphatic acids in solution or in the liquid state are very similar and do not contain sufficient data for the characterization of individual members. This is characteristic for compounds with long alkane chains (see Alkanes).

Table II-106 γCH_2 r frequencies in carboxylic acids [40]

| n | Monocarboxylic acid $\text{CH}_3(\text{CH}_2)_n\text{COOH}$ | Dicarboxylic acid $\text{HOOC}(\text{CH}_2)_n\text{COOH}$ | n -Alkane $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$ |
|-----|--|--|--|
| 0 | | | 822 |
| 1 | 807 | | 748 |
| 2 | 750 | 804 | 732 |
| 3 | 731 | 751 | 728 |
| 4 | 727 | 733 | 726 |
| 5 | 721 | 731 | 723 |
| 6 | 721 | 726 | 722 |
| 7 | 721 | 726 | 720 |
| 8 | 721 | 722 | 720 |
| 12 | | 727 721* | — |

* [37]

The spectra represent mixtures of conformational isomers. In the crystalline state, however, the infrared spectra are drastically changed. It has been shown that in the crystalline state the hydrocarbon chain exists in a single *trans*-zigzag conformation as in alkanes. Under these conditions, the spectra show a number of bands characteristic for various members of the homologous series. In the liquid state these bands are replaced by broad bands identical to those of spectra recorded in solution. Changes between the liquid and crystalline state are influenced to a great extent by the symmetry of the form imposed by the elementary cell. In this regard, the occurrence of polymorphism in acids has to be kept in mind in interpretations of their spectra [38]. Each crystalline modification has its own spectrum [25, 26, 39]. Fig. II-94 shows the spectrum of the β -modification of stearic acid (film), along with that of $\alpha \rightarrow \beta$ forms of stearic acid recrystallized from acetone at 0°C (nujol) [26]

Fig. II-94 Infrared spectrum of crystalline stearic acid. Solid line — β modification, dotted line — mixture of α and β modifications [26]

In the acid series with 2–12 carbon atoms, the same phenomena have been observed. Here too, differences between even- and odd-numbered members have been noticed [25, 40].

In spectra of crystalline aliphatic acids with chains longer than 12 carbon atoms, a progression of bands between 1180 and 1350 cm^{-1} has been observed. This progression is characterized by the uniformity of distances

and intensities. (The bands do not occur in solution [26]). Lauric acid (C_{12}) shows three bands in this region. The lower frequency band occurs at 1195 cm^{-1} . Heneicosanoic acid (C_{21}) shows nine bands, the first occurring at 1181 cm^{-1} . The progressive increase in bands in saturated acids with 12–21 carbon atoms is shown in Fig. 11-17 [26]. Characteristic features have also been noticed in lower acids [25].

In C_{16} – C_{19} , the number of bands seems to increase by one for each CH_2 group. Because the higher frequency region overlaps with the C–O stretching vibration region (very strong absorptions), the limit of the progression is not easy to determine. Assignments are the same as in alkanes: coupling between twisting (*t*) and wagging (*w*) vibrations of the adjacent methylene groups. On chain substitution, the regular pattern of the bands disappears. In elaidic acid, with a *trans* configuration, the two saturated parts of the chain behave somewhat independently and the spectrum is similar to that of lauric acid [26].

d. Acids branched in the α -position. Saturated carboxylic acids branched in the α -position do not show the strong frequency at 1110 cm^{-1} characteristic for the CH_2 group adjacent to the carboxyl. The strong band at 1235 cm^{-1} , occurring in nonbranched acids at 1282 cm^{-1} is considered characteristic in this case.

In methylhexanoic and methyloctanoic acids branched in the 2-, 3-, 4-, and 5-positions, the frequency decreases from 1235 to 1210 cm^{-1} . The position of this band was correlated with chain branching [31].

B. UNSATURATED ACIDS WITH DOUBLE BONDS

1. α,β -Unsaturated acids

a. $\nu\text{C}=\text{O}$ vibration. The mean frequency of the $\nu\text{C}=\text{O}$ stretching vibration in α,β -unsaturated acids $\text{R}-\text{CH}=\text{CH}-\text{COOH}$ is 1690 cm^{-1} in the dimer and 1718 cm^{-1} in the monomer (dilute solution in CS_2 or CCl_4) [19]. Acrylic and metaacrylic acids absorb at 1705 and 1700 cm^{-1} , respectively [9] and the higher members, in the range 1690 – 1700 cm^{-1} .

The decrease in frequency, cf. the corresponding saturated acids, is because of conjugation of the double bond with the carboxyl group.

In α,β -unsaturated acids, the force constant of the $\text{C}=\text{O}$ bond is affected on one hand by the *I* effect of the double bond and on the other hand by the conjugative effect acting in the opposite direction.

The *I* effect tends to increase the $\text{C}-\text{O}$ bond order, whereas the conjugative effect tends to lower it (446). The predomination of the conjugative effect can be seen from the low acidity constant [11], cf. a pure *I* effect (see Halogenated Acids).

In crotonic acid (447) the *I* effect of the methyl group enhances the conjugative effect, reducing still further the $\text{C}-\text{O}$ bond order. The $\nu\text{C}=\text{O}$ fre-

quency decreases accordingly. In *trans*-cinnamic acid the stronger conjugation lowers the frequency to 1680 cm^{-1} [9] (Table II-167).

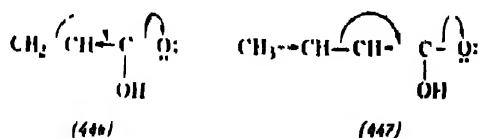


Table II 167 Characteristic frequencies (cm^{-1}) in α,β -unsaturated acids

| Acid | ν_{CO} (in CCl_4) | $\nu_{\text{C}=\text{C}}$ (in CCl_4) | Out-of-plane CH deformation (in CS_2) | |
|---|--|--|---|------------|
| | | | <i>trans</i> | <i>cis</i> |
| $\text{CH}_2=\text{CH}-\text{COOH}$ | 1705* | | | — |
| $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOH}$ | 1700* | | — | — |
| $\text{CH}_3-\text{CH}=\text{CH}-\text{COOH}$ (<i>trans</i>) | 1694 | 1651 | 970 | — |
| $\text{CH}_3-\text{CH}=\text{CH}-\text{COOH}$ (<i>cis</i>) | 1692 | 1639 | | 818 |
| $\text{CH}_3-(\text{CH}=\text{CH})_2-\text{COOH}$ (<i>trans</i>) | 1702 | 1639, 1613 | 998 | — |
| $\text{CH}_3-(\text{CH}=\text{CH})_2-\text{COOH}$ (<i>cis-trans</i>) | 1683 | 1627, 1601 | 990, 994 | — |
| $\text{CH}_3-(\text{CH}=\text{CH})_2-\text{COOH}$ (<i>trans-cis</i>) | 1687 | 1636, 1600 | 996, 958 | 837 |
| $\text{CH}_3-(\text{CH}=\text{CH})_2-\text{COOH}$ (<i>cis-cis</i>) | 1691 | 1620, 1598 | | 829 |
| $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{COOH}$ (<i>trans</i>) | 1680** | | | |
| $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{COOH}$ (<i>cis</i>) | 1702 1700*** | | | |
| $\text{C}_{18}\text{H}_{35}-\text{CH}=\text{CH}-\text{COOH}$ (<i>trans</i>) | 1693**** | 1653 | 980 | — |
| $\text{C}_{18}\text{H}_{35}-\text{CH}=\text{CH}-\text{COOH}$ (<i>cis</i>) | | 1645 | | 825 |

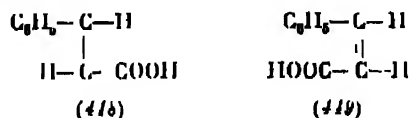
* Liquid.

** 1699 cm^{-1} [42], 1713 m dioxane [9].

*** [42].

**** [43].

In *cis-trans* isomers small differences in frequency are observed (Table II-167). They are larger in cinnamic acids.



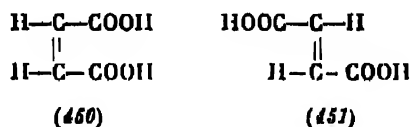
cis-Forms (449) absorb at 1702 , 1707 , and 1709 cm^{-1} and *trans*-forms (448) absorb at 1699 cm^{-1} [12]. The phenomenon is partially attributable to a secondary steric effect [11] resulting in the disappearance of conjugation in *cis* isomers because of distortion of the carboxyl group out of the plane of the double bond. This interpretation is in line with the higher acidity of *cis*- α,β -unsaturated acids, cf. the *trans* isomers.

In higher aliphatic α,β -unsaturated acids, the ν_{CO} frequency lies in the range 1692 – 1700 cm^{-1} for both stereoisomers [43, 11].

On extension of the conjugated system the $\Delta\nu_{\text{CO}}$ increment for each

additional double bond becomes smaller. The phenomenon is similar to that in α,β -unsaturated carbonyl compounds (see Polyenic Aldehydes). Table II-167 includes νCO and $\nu\text{C}=\text{C}$ frequencies of some α,β -unsaturated aliphatic acids with several double bonds [45].

Dicarboxylic unsaturated acids with the two carboxyl groups directly attached to the double bond show higher νCO frequencies for *cis* forms than for *trans* isomers. Maleic acid (450) absorbs at 1705 cm^{-1} , and fumaric acid (451), at 1680 cm^{-1} [9].



The equilibrium constant varies in the same direction. At 25°C it is 9.5×10^{-4} for fumaric acid and 142×10^{-4} for maleic acid [46]. (The same differences in frequency are observed both in nitriles and esters of α,β -unsaturated dicarboxylic acids).

b. $\nu\text{C}=\text{C}$ vibration. In α,β -unsaturated acids, the frequency and the intensity of the $\nu\text{C}=\text{C}$ band are used for the identification of the position and steric configuration of the double bond with respect to the carboxyl group.

Acids with an α,β -double bond show a single $\nu\text{C}=\text{C}$ band at $1630\text{--}1660\text{ cm}^{-1}$. The number of bands is larger in compounds with conjugated double bonds (Table II-167). *trans*-Isomers have higher frequencies than *cis* isomers (by $10\text{--}20\text{ cm}^{-1}$). This fact has been used in assignments of configuration in a number of α,β -unsaturated acids [13, 45] (Table II-167).

c. CH deformation vibration. The frequency of the out-of-plane CH deformation mode, characteristic for alkenes is $970\text{--}990\text{ cm}^{-1}$ in *trans* isomers and ca. 820 cm^{-1} in *cis* isomers [45].

In *trans*-2-octadecanoic acid, the out-of-plane deformation band occurs at 980 cm^{-1} in the solid state and at 860 cm^{-1} in the liquid state. The *cis* isomer absorbs at 825 cm^{-1} [13].

2. Unsaturated acids with isolated double bonds

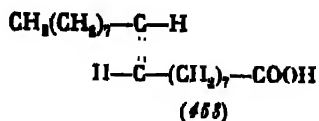
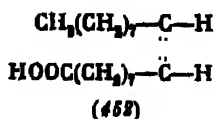
Infrared spectra of unsaturated acids with isolated double bonds show the characteristics of the two functional groups. We limit our discussion to some problems connected with fatty acids because of their great practical value.

Frequencies arising from the carboxyl group are essentially the same as in saturated alkyl carboxylic acids and have been discussed above ($\nu\text{CO}=1710 \pm 10\text{ cm}^{-1}$).

The hydrocarbon group shows characteristic frequencies of $\text{C}-\text{C}$, CH_2 , CH_3 , and CH_2COOH groups.

a. $\nu\text{C}=\text{C}$ vibration. In *cis*-alkenes this vibration gives rise to a weak absorption at 1660 cm^{-1} . In *trans* isomers the band is extremely weak or does not occur at all. Of the two isomeric acids with 18 carbon atoms and

a double bond in the middle of the chain, only the *cis* isomer (oleic acid 452) shows the $\nu\text{C}=\text{C}$ absorption. The *trans* isomer (elaidic acid 453) does not show any absorption in this region.



On comparing spectra of C_{18} acids with one, two, and three double bonds (elaidic, oleic, linoleic and linolenic) (Fig. II-95) an increase in band intensity with the number of double bonds is observed. Position and intensity of this band point out the following configurations: *cis* for oleic acid (452), *cis-cis* for linoleic acid (454), and *cis-cis-cis* for linolenic acid (455) [43, 47].

However, this absorption is not suitable for analytical purposes because of superimposition with the very strong absorption of the $\text{C}=\text{O}$ bond. More suitable for the identification of *cis-trans* isomerism is the band arising from the out-of-plane CH deformation vibration in the 960 cm^{-1} region.

b. **CH vibrations.** Both stretching and deformation modes are of value in investigating the nature of unsaturation. Saturated and unsaturated νCH bands can be used to determine the number of double bonds, i.e., the degree of unsaturation. Deformation bands are also used to establish *cis-trans* isomerism.

1. **Stretching vibrations.** In the νCH stretching vibration region, unsaturated acids are characterized by vibration of the alkenic $=\text{C}-\text{H}$ bond, giving rise to absorptions above 3000 cm^{-1} and by stretching vibrations of CH_2 and CH_3 from the saturated part of the chain. In *cis* isomers of C_{18} fatty acids,

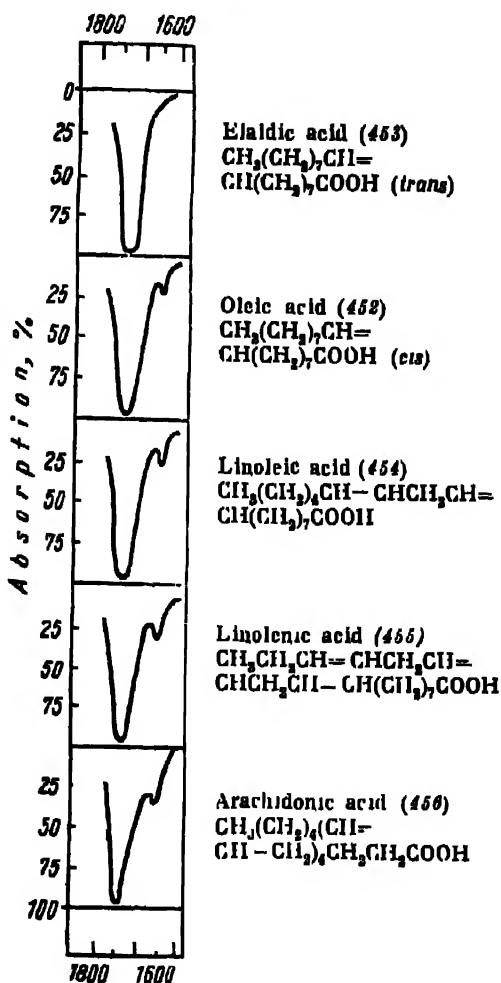


Fig. II-95 $\nu\text{C}=\text{C}$ band in unsaturated fatty acids.

(oleic, linoleic, and linolenic) the $=CH$ stretching mode gives rise to a band at 3020 cm^{-1} . The intensity of this band increases with the number of double bonds [43]. The increase in intensity of the $=CH$ absorption is accompanied by a decrease in intensity of the CH_2 absorptions (2920 and 2850 cm^{-1}) and of the terminal CH_3 absorptions (2920 and 2870 cm^{-1}). Relative intensity variations of $\nu=C-H$ and νCH_2 bands are used for the determination of the degree of unsaturation in acids [43].

If $O.D.(A)$ is the optical density of the 3020 cm^{-1} band and $O.D.(B)$ that of the 2920 cm^{-1} band, on plotting the ratio

$$\frac{O.D.(B)}{O.D.(B) - O.D.(A)}$$

against the number of double bonds, a straight line is obtained in the case of C_{18} acids with one to three double bonds (Fig. II-96).

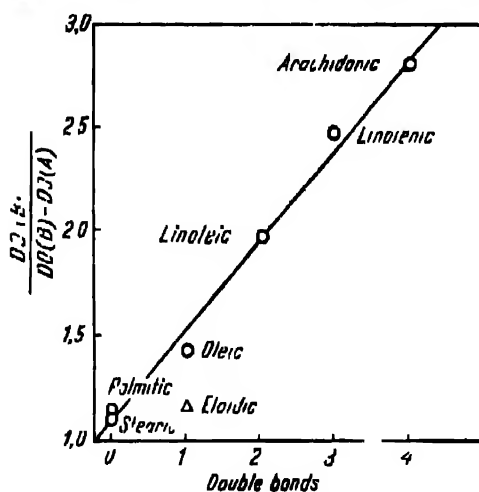


Fig. II-96 Variation of optical density with the number of double bonds in unsaturated fatty acids.

Elaidic acid (the *trans* isomer) absorbs in the νCH region at 2995 , 3015 , and 3030 cm^{-1} . It does not fall on the line.

2. $C-H$ deformation vibrations. Out-of-plane $C-H$ deformation vibrations of the $CH=CH-$ group are the most characteristic ones both for determining *cis-trans* isomerism (see Alkenes) and the degree of unsaturation. Absorptions of *trans* isomers correspond to those of *trans* disubstituted ethylenes ($965-975\text{ cm}^{-1}$). *cis* isomers have absorptions of variable frequency at ca. 690 cm^{-1} . Figure II-97 shows the CH deformation region in oleic, elaidic, and stearic acids. It can be seen that only elaidic acid (*trans*) has an absorption at 960 cm^{-1} .

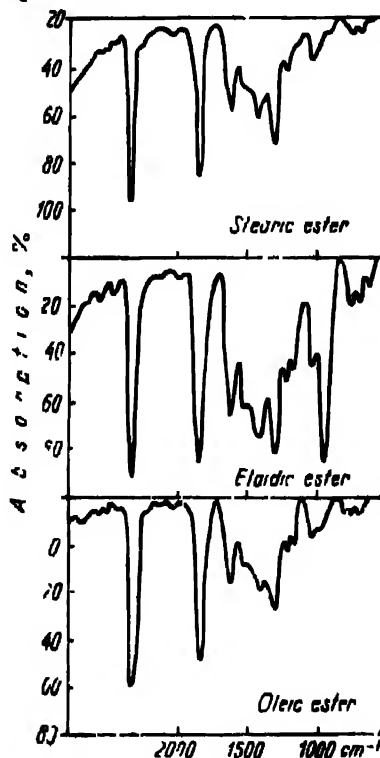
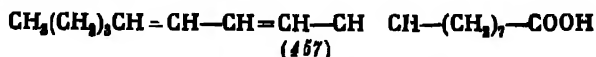


Fig. II-97 Infrared spectra of esters of stearic, elaidic, and oleic acids in the CH deformation mode region.

The utilization of the *trans* δ CH band for analytical purposes in the determination of *trans* double bonds is more accurate than current chemical methods [47]. The method is widely used to study geometrical isomerism in C_{18} fatty acids with multiple double bonds [47, 48–51]. In stereoisomeric linoleic acids, the *trans-trans* isomer absorbs at 988 cm^{-1} . The *cis-trans* isomer shows two bands: a strong one at 982 cm^{-1} and a medium one at 950 cm^{-1} . The *cis-cis* isomer has a very weak absorption at 913 cm^{-1} [51].

In α -eleostearic (9-*cis*-11-*trans*-13 *trans* octadecatrienoic) acid (457) with conjugated double bonds



the CII deformation band is three times stronger than in elaidic acid [50]. This band enables the quantitative determination of stereoisomers in a mixture, using pure isomers as standards [52, 53].

Some of the most important current practical applications are control of hydrogenation of vegetable oils, control of oxidation, and autooxidation of fats. In the latter processes the 3500 cm^{-1} (νOH) region is of special value [47, 54, 55].

C. UNSATURATED ACIDS WITH TRIPLE BONDS

In acetylenic acids with an α,β -triple bond, the νCO frequency is lower than in acids with a double bond in the same position. In most cases the absorption occurs between 1680 and 1690 cm^{-1} . In dicarboxylic acids the absorption is slightly higher. For example, acetylene dicarboxylic acid absorbs at 1700 cm^{-1} (45).

The decrease in νCO frequency in acetylenic acids cannot be explained by the $-I$ effect of the ethynyl group (which should increase the frequency). Neither can it be explained by a conjugative effect, which in this case is weaker. It has to be related to the stronger s -character of the $\equiv\text{C}-\text{COOH}$ bond as a result of the sp hybridization of the acetylenic carbon atom.

The extension of the conjugated triple bonds system does not result in a progressive decrease in frequency (Table II-168). If the triple bond is isolated from the carboxyl group, the νCO frequency has the same value as in saturated compounds.

Table II-168 Characteristic frequencies in acids with triple bonds* [45]

| Acid | $\nu\text{C}\equiv\text{C}$ | $\nu\text{C}=\text{O}$ | $\nu\text{C}-\text{C}$ |
|--|-----------------------------|------------------------|------------------------|
| $\text{CH}_3-\text{C}\equiv\text{C}-\text{COOH}$ | 2246 <i>m</i> | 2140 <i>w</i> | 1684 |
| $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{COOH}$ | 2258 <i>m</i> | — | 1690 |
| $\text{CH}_3-(\text{C}\equiv\text{C})_2-\text{COOH}$ | 2270 <i>s</i> | 2180 | 1688 |
| $\text{CH}_3-(\text{C}\equiv\text{C})_3-\text{COOH}$ | 2210 <i>s</i> | 2135 | 1694 |
| $\text{C}_6\text{H}_5(\text{C}\equiv\text{C})_2-\text{COOH}$ | 2200 <i>s</i> | 2130 | 1684 |
| $\text{HC}\equiv\text{C}-\text{CH}_2-\text{C}\equiv\text{C}-\text{COOH}$ | 2248 | 2215 | 1693 |
| $\text{HOOC}-\text{C}\equiv\text{C}-\text{COOH}$ | — | — | 1700 |
| $\text{CH}_3-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{COOH}$ | 2224 <i>s</i> | 2190 <i>s</i> | 1667 1618 <i>s</i> |
| <i>trans</i> | | | |
| $\text{CH}_3-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{COOH}$ | 2219 <i>m</i> | — | 1692 1615 |
| <i>cis</i> | | | |

* In carbon tetrachloride.

$\nu\text{C}\equiv\text{C}$ vibrations. Conjugation results in a rise in intensity of the $\nu\text{C}\equiv\text{C}$ band, as in the case of acetylenic hydrocarbons [45]. The bands occur at 2235–2260 cm^{-1} in compounds with a single triple bond and at 2200–2270 cm^{-1} in polyacetylenes with two or three triple bonds. In the centrosymmetric acetylenedicarboxylic acid, the $\nu\text{C}\equiv\text{C}$ absorption does not occur.

D. AROMATIC ACIDS

a. $\text{C}=\text{O}$ stretching vibration. Conjugation of the carboxyl group with the aromatic ring results in a larger decrease in νCO and νOH frequencies than in α , β -unsaturated acids. Depending on experimental conditions, absorptions of either the monomeric or the dimeric carboxyl group can be determined [9, 56]. In benzoic acid, the νCO absorption of the monomeric form (dilute solution in carbon tetrachloride) occurs at 1744 cm^{-1} . Under the same conditions the dimeric form absorbs at 1697 cm^{-1} . The frequency is sensitive to the nature of the solvent, and small differences are observed in various recordings. In general, in *meta*- and *para*-substituted benzoic acids, the νCO frequencies of monomeric forms lie in the range 1737–1752 cm^{-1} and those of the dimers occur at 1690–1709 cm^{-1} [56]. Frequencies vary with the nature of the substituent. They decrease in molecules with electron-releasing substituents, due to their strong $+E$ effect, increasing the electron density at the carbon atom of the COOH group. In the case of substituents lowering the electron density at the same atom ($-I$ and $-E$ effects) the frequencies increase. In many substituted aromatic acids, a linear relationship has been observed between the frequency of the νCO (and νOH) frequency of the monomeric or dimeric carboxyl group and the effect of substituents expressed by Hammett- σ values [57, 58]. In benzoic acids substituted in the *para*-position with groups with negative Hammett- σ values (NR_2 , OC_6H_5 , CH_3), the lowest frequency is observed in compounds with the largest negative σ -value (NH_2). For positive values the frequency increases proportionally (Table II-169) [59]

Table II-169 Relationship between frequency (cm^{-1}) and Hammett- σ constants in substituted benzoic acids

| Substituent | $\nu\text{C}=\text{O}$ | | Hammett- σ |
|---------------------------|-----------------------------------|-------------------------|-------------------|
| | Monomer in CH_2OH | Dimer in CCl_4 | |
| <i>p</i> - NH_2 | 1690 | — | −0.660 |
| <i>p</i> - OCH_3 | 1695 | 1691 | −0.268 |
| <i>p</i> - CH_3 | 1700 | 1693 | −0.170 |
| H | 1705 | 1696 | 0.0 |
| <i>p</i> -Br | 1710 | 1698 | +0.232 |
| <i>p</i> -Cl | 1713 | 1699 | +0.227 |
| <i>m</i> -Cl | 1715 | 1701 | +0.379 |
| <i>m</i> - NO_2 | 1723 | 1705 | +0.710 |
| <i>p</i> - NO_2 | 1720 | 1707 | +0.778 |

logenobenzoic acids show two absorptions for the monomeric carboxyl. The dimer has a single band (Table II-170).

The same parallelism has been observed between the νOH frequency and the dissociation constant of the monomeric acid [2].

ortho-Substituted compounds show a special behaviour due to interactions between the two adjacent substituents. *o*-Toluic, *o*-nitrobenzoic, and *o*-acetoxybenzoic acids have a single νCO absorption. *o*-Methoxy- and *o*-ha-

In monomeric *o*-methoxybenzoic acid, the doubling of band is attributable to the intramolecularly bonded form (460), coexisting with molecules with free carboxyl groups (458) or (459). Conformation (460) is assigned the lower frequency (1751 cm^{-1}). It has the highest intensity. Form (459) or (458)

Table II-170 Characteristic frequencies (cm^{-1}) in substituted benzoic acids [56]

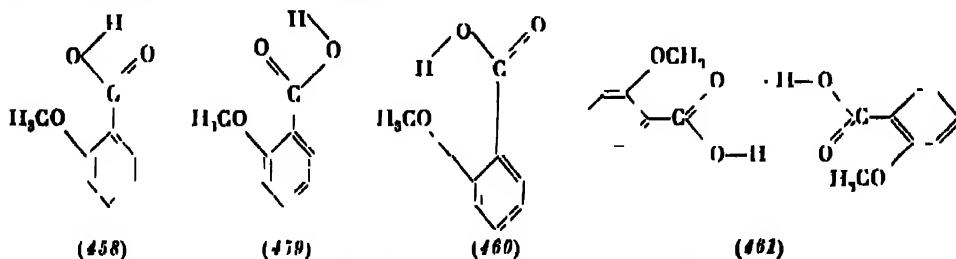
| Substituent | Monomer* νCO | Dimer* | |
|---------------------------------------|----------------------------|----------------|----------------|
| | | νCO | νOH |
| <i>meta</i> $\text{N}(\text{CH}_3)_2$ | 1740 | 1693 | 3541 |
| | OCH_3 | 1741 | 1698 |
| | CH_3 | 1742 | 1698 |
| | — | 1744 | 1697 |
| | Hal (mean) | 1748 | 1703 |
| | NO_2 | 1752 | 1709 |
| <i>para</i> | OCH_3 | 1737 | 1691 |
| | CH_3 | 1740 | 1697 |
| | Hal (mean) | 1745 | 1698 |
| | NO_2 | 1752 | 1707 |
| | OCOCCH_3 | 1752 | 1707 |
| <i>ortho</i> | OCH_3 | 1751, 1760** | 1702*** |
| | CH_3 | 1742 | 1696 |
| | Hal (mean) | 1756, 1738 | 1708 |
| | NO_2 | 1760 | 1715 |
| | OCOCCH_3 | 1747 | 1702 |

* Solution in CCl_4 .

** Shoulder.

*** Very weak absorption.

gives rise to a weak absorption, occurring as a shoulder at 1760 cm^{-1} . The dimer, with structure (461), absorbs at 1702 cm^{-1} . This interpretation, based in intensity variations with solvent and on analogy with other molecules showing an *ortho*-effect is preferred to the interpretation based on a Fermi resonance (by analogy with some ketones) [60, 61].

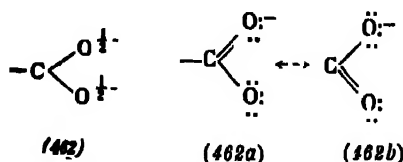


b. Other characteristic frequencies of the carboxyl group. Substituted benzoic acids show characteristic absorptions at 1410–1435 cm^{-1} and 915–935 cm^{-1} assigned to the coupling of the OII deformation mode with the $\text{C}=\text{O}$ stretching mode. In benzoic acid these vibrations give rise to absorptions at 1420 and 935 cm^{-1} . The absorption at 1280–1300 cm^{-1} (in benzoic acid, at 1287 cm^{-1}) is considered characteristic of the dimeric forms [9, 28, 32].

Naphthalene carboxylic acids absorb at 1118 and 893 cm^{-1} (α -isomer) and 1427 and 943 cm^{-1} (β -isomer) [9, 32].

E. THE CARBOXYLATE ION

Isovalent conjugation (462a, 462b) in the carboxylate ion results in a uniform partition of electrons between the three atoms (462). The two bond orders are equal, as well as the interatomic distances (1.27 Å). These distances are intermediate between the length of a simple C—O bond and a C=O double bond. Consequently, the frequencies of these bonds are expected to have intermediate values between $\nu\text{C}=\text{O}$ and $\nu\text{C}-\text{O}$. The $-\text{COO}^-$ group (carboxylate ion) has an asymmetric stretching vibration with a frequency lying in the range



1550—1610 cm^{-1} and a symmetric stretching vibration with frequencies between 1300 and 1100 cm^{-1} . The identification of the symmetric vibration is rather difficult, because of the large number of bands occurring in this region [63].

When carboxylic acids are converted to alkaline salts, the four bands of the carboxyl group vanish, being replaced by the two bands of the COO^- group. The intensity of the band arising from the asymmetric vibration is about three times greater than in free acids because of the more polar character of this group [30]. The transformation of acids to salts is advantageous, allowing, among other things, the more accurate identification of CH vibrations, obscured in the case of dimeric acids.

Table II-171 shows frequencies arising from the asymmetric stretching mode of the $-\text{COO}^-$ group in sodium salts of various aliphatic mono- and dicarboxylic acids (in KBr) [30].

Table II-171 Asymmetric stretching vibration (cm^{-1})
in the carboxylate ion* [30]

| Monocarboxylic acid | ν_{asym} | Dicarboxylic acid | ν_{asym} |
|---------------------|---------------------|-------------------|---------------------|
| Acetic | 1578 | Oxalic | 1616 |
| Propionic | 1571 | Malonic | 1595 |
| Butyric | 1565 | Succinic | 1575 |
| Valeric | 1569 | Glutaric | 1577 |
| | | Adipic | 1576 |
| | | Pimelic | 1580 |

* In KBr.

The symmetric vibration occurring at ca. 1400 cm^{-1} is not characteristic. The nature of the hydrocarbon group increases or decreases this frequency

through an inductive or conjugative effect. Sodium benzoate shows the absorptions of the carboxylate ion at 1549 and 1415 cm^{-1} [64]. Along with these, only characteristic absorptions of the monosubstituted benzene ring occur in the spectrum (3060, 1599, 714, and 673 cm^{-1}). In ring-substituted benzoates, the frequency varies with the nature of the substituent. Here too, a linear relationship between frequency and the Hammett- σ constant has been observed. The nature of the cation affects the frequency very little. In this regard, it has been shown that there is a linear relationship between the electronegativity of the mono- or divalent cation and the asymmetric frequency of the carboxylate ion [65–67].

Confirmation of the assignments of the COOH, COOD, and COO^- bands [68] has been made by observation of their appearance and disappearance in acidic (HCl, DCl) and basic (NaOH, NaOD) media.

F. SUBSTITUTED CARBOXYLIC ACIDS

1. Halogenated acids

a. Aliphatic acids.

1. νCO vibration. The $\nu\text{C}=\text{O}$ frequency in halogenated acids depends on the position of the halogen atom. In α -halogenated compounds, the νCO frequency is higher than in the corresponding unsubstituted acids. This is attributable to the $-I$ effect of the electronegative halogen atom, resulting in a shift of electrons as in (462). In such structures the C–O bond order (and frequency) rise; conversely, the O–H bond becomes weaker and the νOH frequency decreases. The decrease in frequency parallels the rise in acidity constant. There is a linear relationship between $\Delta\nu\text{OH}$ and pK_a [69]. It is well known that the intensity of the inductive effect falls along the chain. Consequently, in halogenated acids with the halogen atom in a more remote position, the frequency returns to normal; for example, β -chloropropionic acid and 9-bromostearic acid absorb at 1710 cm^{-1} [26]. However, α -chloropropionic acid absorbs at 1730 cm^{-1} [9].

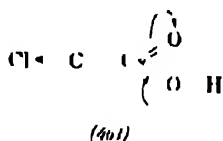


Table II-172 νCO frequencies (cm^{-1}) in α -halogenoacetic acids [69]

| Acid | νCO (in CCl_4) | Dissociation constant $\cdot 10^4$ |
|----------------------------|--|---------------------------------------|
| CH_3COOH | 1721 | 1.86 |
| ICH_2COOH | 1721 | 74 |
| BrCH_2COOH | 1730 | 138 |
| ClCH_2COOH | 1736 | 155 |
| Cl_2CHCOOH | 1751 | 5000 |
| Cl_3CCOOH | 1764 | 130000 |
| F_3CCOOH | 1776 | — |

In α -halogenoacetic acids successive replacement of α -hydrogen atoms by halogens results in a progressive increase in frequency for each additional halogen. The effect is cumulative [69–71] (Table II-172). The acidity rises in the same direction.

Similar variations in frequency also take place in the vapor phase (monomeric carboxyl). Monochloroacetic acid absorbs at 1794 cm^{-1} , 10 cm^{-1} higher than acetic acid (1785 cm^{-1}).

The largest shifts are observed in fluoro acids (with the most electronegative halogen atom). Trifluoroacetic acid absorbs at 1843 cm^{-1} in the vapor phase (monomer), at 1781 cm^{-1} in solution or cold vapors, and at 1776 cm^{-1} in the liquid state (Table II-173) [71].

Table II-173 νCO and νOH frequencies (cm^{-1}) in fluoroacetic acids [71]

| Fluoroacetic acid | Monomer | | | Dimer | | | |
|-----------------------------------|------------------------|----------|----------------|------------------------|--------|----------------|-----------|
| | $\nu\text{C}=\text{O}$ | | νOH | $\nu\text{C}=\text{O}$ | | νOH | |
| | Hot vapor | Solution | Hot vapor | Solution | Liquid | Liquid | Vapor |
| $\text{F}_3\text{C}-\text{COOH}$ | 1843 | 3498 | 3587 | 1781 | 1776 | 3280 | 3141–3150 |
| $\text{F}_2\text{CH}-\text{COOH}$ | 1815 | 3520 | 3587 | 1751 | 1739 | 3240 | 3100–3180 |
| FCH_2-COOH | 1806 | 3520 | 3587 | 1737 | 1729 | 3310 | 3120–3140 |

The coexistence of conformational isomers is apparent from the increased number of bands. In monomeric fluoroacetic acid, bands at 1806 and 1783 cm^{-1} were assigned to *anti* (*trans*) and staggered *syn* isomers [72, 73].

2. νOH Vibrations. In the monomeric acid, νOH absorptions occur between ca. 3500 and 3600 cm^{-1} (Table II-173).

In fluoroacetic acid (hot vapors), the free νOH absorption occurs at 3587 cm^{-1} [72, 74]. In dilute carbon tetrachloride solution, the frequency decreases to 3498 cm^{-1} [75]. In the liquid state a very broad band occurs between 3100 and 3300 cm^{-1} . In general, the νOH frequency in halogenated acids is lower than in the corresponding saturated acids; for example, trichloroacetic acid absorbs at 3504 cm^{-1} and acetic acid at 3533 cm^{-1} .

b. **Aromatic acids.** *meta*-Halogenobenzoic acids have slightly higher νCO frequencies than benzoic acid. In *para* isomers $-I$ and $+E$ effects cancel each other, and the frequency returns to normal (Table II-174).

In *ortho*-halogenobenzoic acids, a doubling of the νCO band is observed (in monomers). The first component of the doublet has a slightly lower frequency than in benzoic acid, whereas the second component has an appreciably higher frequency. The distance between the components is constant (ca. 17 cm^{-1}) in all *o*-halogenated acids. However, the relative intensity of the two bands varies with the nature of the halogen atom [56]. Table II-175 shows frequencies and apparent extinction coefficients ($\epsilon^{(a)}$) of νCO absorptions in *o*-F, *o*-Cl, *o*-Br, and *o*-I benzoic acids in carbon tetrachloride solution (0.0015 M).

Band shapes are seen in Fig. II-98.

Absorptions with frequencies at ca. 1736 cm^{-1} were assigned to conformation (464) and those at 1755 cm^{-1} to conformation (465).

It is assumed that the dimer has conformation (467). $\Delta\nu$ monomer-dimer is approximately 45 cm^{-1} . A conformation with intramolecular (chelate type

Table II-174 νCO and νOH frequencies (cm^{-1})
in halogenobenzoic acids* [56]

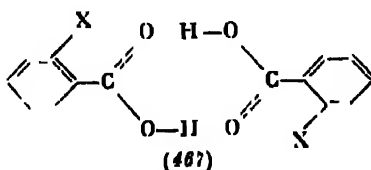
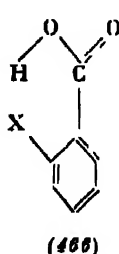
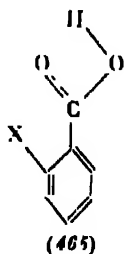
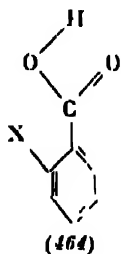
| Halogen | Monomer** | Dimer** | |
|----------------|----------------|----------------|----------------|
| | νCO | νCO | νOH |
| <i>meta</i> F | 1718 | 1703 | 3536 |
| Cl | 1748 | 1703 | 3535 |
| Br | 1748 | 1702 | 3535 |
| <i>para</i> F | 1745 | 1699 | 3538 |
| Cl | 1745 | 1698 | 3536 |
| Br | 1745 | 1698 | 3536 |
| <i>ortho</i> F | 1755, 1739 | 1707 | 3529 |
| Cl | 1756, 1738 | 1706 | 3527 |
| Br | 1757, 1738 | 1711 | 3528 |
| I | 1753, 1736*** | 1708 | 3530 |

* Benzoic acid $\nu\text{CO}=1744\text{ cm}^{-1}$ (monomer); 1697 cm^{-1} (dimer); $\nu\text{OH}=3540\text{ cm}^{-1}$.

** Solution in CCl_4 .

*** Shoulder.

bonds) (466) is considered unlikely because of unique νOH bands at ca. 3528 cm^{-1} , corresponding to a free OH.



6-Chlorosalicylic acid, where the $\text{C}=\text{O}$ group forms a chelate bond with the phenolic hydroxyl, shows two bands: 3508 cm^{-1} (free hydroxyl of the COOH group) and 3431 cm^{-1} (bonded hydroxyl) [56, 76].

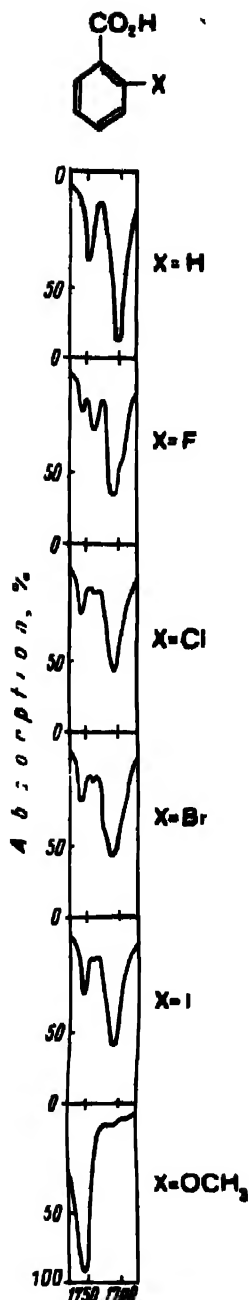


Fig. 11-98 Infrared spectra of *o*-halogenobenzoic acids in the $\text{C}=\text{O}$ stretching vibration region.

Table II-175 νCO frequencies and intensities in *o*-halogenobenzoic acids

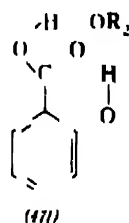
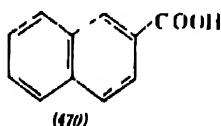
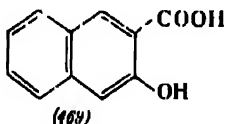
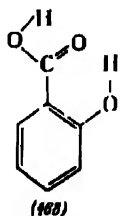
| Halogen | F | | Cl | | Br | | I | |
|--------------------------------|------|------|------|-------|------|------|------|-------|
| $\nu\text{CO}(\text{cm}^{-1})$ | 1755 | 1739 | 1756 | 1738 | 1757 | 1738 | 1753 | 1736* |
| $\epsilon(\text{a})$ | 155 | 220 | 200 | (105) | 200 | (95) | 230 | (90) |

* Shoulder: in brackets, estimated values.

2. Hydroxy acids

The $-I$ effect of the hydroxyl group in the α -position of aliphatic acids results in an increase in $\text{C}=\text{O}$ frequency; for example, lactic acid absorbs at 1725 cm^{-1} [9]. Because of the possibility of inter- and intramolecular hydrogen bonding when the two groups are in adequate positions, infrared spectra of hydroxy acids represent molecular species resulting from interactions between the hydroxyl and carboxyl groups.

In the case of aromatic acids disubstituted in adjacent positions, large shifts toward lower frequencies are characteristic. Formation of intramolecular hydrogen bonds stabilized by a chelate conjugation results in a decrease in $\nu\text{C}=\text{O}$ frequency to $1650\text{--}1680\text{ cm}^{-1}$. Salicylic acid (468), for example, absorbs at 1665 cm^{-1} in the solid state and at 1680 cm^{-1} in dioxane solution; in 3-hydroxy-naphthalene-2-carboxylic acid (469), the frequency is 35 cm^{-1} lower than in naphthalene-2-carboxylic acid (470) [9].



A 0.0015 M solution of salicylic acid in carbon tetrachloride absorbs at 1698 cm^{-1} (chelated monomer) and at 1663 cm^{-1} (dimer). The distance between the two absorptions is 35 cm^{-1} , significantly smaller than in nonchelated acids ($\Delta\nu = 15\text{ cm}^{-1}$). Ether solutions of salicylic acid show only absorptions arising from form (471), where the OH group is associated with ether molecules. The νCO frequency decreases to 1679 cm^{-1} ($\Delta\nu_{\text{CO}} = 16\text{ cm}^{-1}$), corresponding to the shift in benzoic acid ($\Delta\nu = 18\text{ cm}^{-1}$) [56, 76]. Under these conditions the chelate ring does not open. Substituents in the 3- and 6-positions, adjacent to the chelate ring, affect the CO frequency. In substituted alkylsalicylic acids a parallelism has been observed between frequency shifts and size of the substituent in the 6-position (Table II-176).

The highest frequency is observed in 3-alkylsalicylic acid and is due to the inductive effect of the methyl group. Bulkier alkyl groups (3- and 6-*t*-butyl derivatives) cause an appreciable decrease in frequency, sterically favoring chelate conjugation (shortening of the $\text{OH}\cdots\text{O}$ distance).

The ν_{OH} frequency in nonbonded salicylic acids occurs at $3530 \pm 3 \text{ cm}^{-1}$. It is independent of alkyl substituents in the 3-, 4- and 5- positions but decreases to $3513\text{--}3519 \text{ cm}^{-1}$ in 6-alkyl derivatives [76, 77].

Table II-176 ν_{CO} and ν_{OH} frequencies (cm^{-1}) in alkylsalicylic acids

| Substituent | $\nu_{C=O}^*$ | | ν_{OH} | ν_{CO} (in ether) |
|----------------------|---------------|-------|------------|-----------------------|
| | Monomer | Dimer | Monomer | |
| (H) | 1698 | 1663 | 3530 | 1679 |
| 3-Methyl | 1695 | 1660 | 3531 | 1677 |
| 3- <i>t</i> -Butyl | 1691 | 1657 | 3530 | 1670 |
| 6-Methyl | 1686 | 1650 | 3517 | 1667 (1660)* |
| 3-Methyl-6-isopropyl | 1677 | 1640 | 3514 | 1657 |

* In dilute carbon tetrachloride solution.

Hydroxy acids with the OH group in the γ - or δ -positions form lactones. In these cases the ν_{CO} frequency corresponds to the lactone ring (see Lactones).

3. α -Keto acids

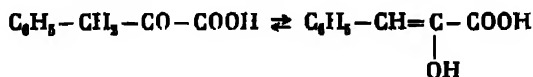
Spectra of α -keto acids show an increase in $\nu_{C=O}$ frequency both in the carbonyl and the carboxyl group because of the $-I$ effect of these functions.

Depending on experimental conditions, the spectra show bands arising either from the monomeric or the dimeric carboxyl [78, 79] (Table II-177).

Table II-177 Characteristic frequencies in α -keto acids [78]

| Acid | Solution in CCl_4 | | | Liquid $\nu_{C=O}$ dimer |
|--|----------------------------|------------------------|------------|--------------------------------|
| | $\nu_{C=O}$ dimer | $\nu_{C=O}$ monomer | ν_{OH} | |
| $\text{CH}_3\text{CO}-\text{COOH}$ | 1725 | 1790 | 3430 | 1725 |
| $\text{CH}_3\text{CH}_2\text{CO}-\text{COOH}$ | 1724 | 1788 | 3428 | 1730 |
| $\begin{matrix} \text{CH}_3 \\ \text{CH}_2 \end{matrix} \text{CH}-\text{CO}-\text{COOH}$ | 1717 | 1786 | 3425 | 1730 |

In phenyl pyruvic acid, enolization results in a more complicated spectrum. The carbonyl ν_{CO} band vanishes and an absorption at 1717 cm^{-1} occurs instead, assigned to the carboxyl group of the α,β -unsaturated acid.



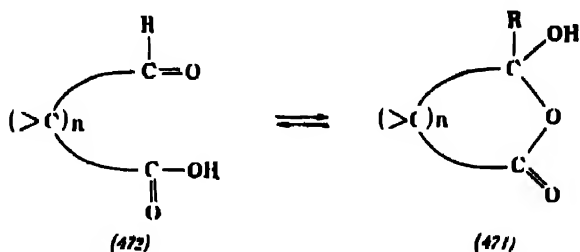
The OH group in the monomeric carboxyl absorbs at ca. 3430 cm^{-1} . The frequency is lower than in saturated acids. This parallels the rise in ν_{CO} frequency as a result of the $-I$ effect of the CO group.

The same effect is observed in α -halogenoacids.

(β -Ketoacids - see Esters).

4. γ -Keto acids

In interpreting spectra of γ -keto acids, the possibility of ring-chain tautomerism ($472 \rightleftharpoons 473$) has to be taken in account.

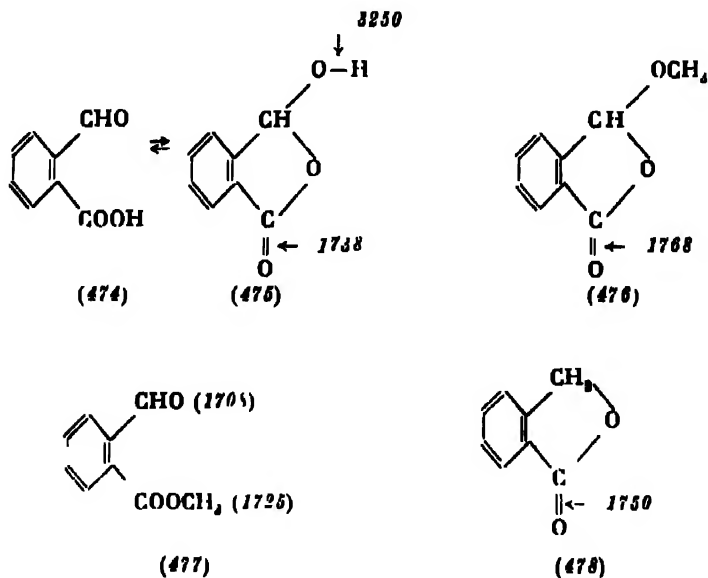


In keto form (472), $\nu\text{C}=\text{O}$ frequencies of the carbonyl and carboxyl groups are those of the corresponding monofunctional derivatives. Infrared spectra show two $\nu\text{C}=\text{O}$ absorptions [15, 80–83].

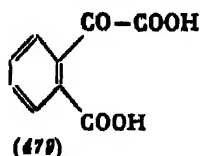
The hydroxylactonic form (lactol) shows a single νCO absorption corresponding to the γ -lactonic ring (473). The absorptions of the carboxyl group disappear, being replaced by absorption of the alcoholic hydroxyl [17].

Absorptions for *o*-phthalaldehydic acid (474) and its esters (476, 477) are indicated on the structures.

In hydroxylactone (475), the νCO frequency is close to that of phthalide (478). Its methyl ester (476) absorbs at much higher frequencies than the ester of the carbonyl form (477).

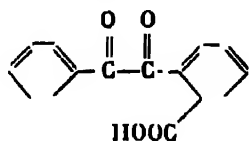


Phthalonic acid (479) (α - and γ -keto acid) shows two νCO bands 1765 and 1725 cm^{-1} . The νOH frequency is 3472 cm^{-1} .

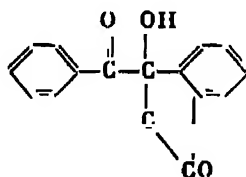


Acetophenone-*o*-carboxylic acid shows a band in the νCO region (1732 cm^{-1}) and another one in the νOH region (3205 cm^{-1}), corresponding to a hydroxylactonic structure.

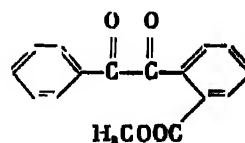
In benzil-*o*-carboxylic acid, the keto form (480) and the hydroxylactonic form (481) absorb at different frequencies. The keto form shows carbonyl bands and aromatic carboxyl bands, very close to each other. In the hydroxylactonic form (481) one band corresponds to the aromatic carbonyl group (1692 cm^{-1}) and the other with a much higher frequency, corresponds to the $\text{C}=\text{O}$ group in hydroxylactone (1745 cm^{-1}) [15].



νCO , cm^{-1} 1695
1683
(480)



1692 (ketone)
1745 (lactone)
(481)



1680 (ketone)
1713 (ester)
(482)

In the phthalide series, νCO frequencies lie in the range 1740–1770 cm^{-1} , whereas aromatic esters absorb at 1710–1730 cm^{-1} [15].

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CHAPTER 8

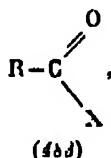
FUNCTIONAL DERIVATIVES OF CARBOXYLIC ACIDS

Functional derivatives of carboxylic acids can result by the modification of both OH and CO group of the carboxyl. These changes are reflected in the infrared spectrum by the disappearance of characteristic bands (OH or CO) and the appearance of bands arising from the new groups and by specific shifts in frequency of the unchanged group.

In many derivatives changes take place in the OH group. As a result large changes in the C=O force constant occur. This explains the wide spread of CO absorptions ($1650\text{--}1900\text{ cm}^{-1}$) in functional derivatives of acids.

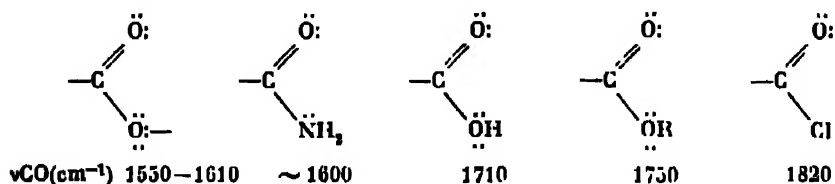
Among factors affecting the force constant, electron distribution in the carbon-oxygen bond is, obviously, of primary importance. This distribution is affected by electronic effects (*I* or *E*) and by field effects. Physical state, solvent, mass of the atoms in the α -position, and vibrational coupling result in much smaller frequency shifts and do not prevent the identification of the functional group [1].

In functional derivatives



X is a halogen atom or a group containing oxygen or nitrogen. The most electronegative halogen atom displays its $-I$ effect, increasing the carbon-oxygen bond order, hence the force constant and the frequency of the $\nu\text{C}=\text{O}$ vibration. In functional derivatives with oxygen or nitrogen atoms, both having an $-I$ effect, the unshared electrons of these atoms are involved in conjugation with the C=O group, which loses its double bond character and gives rise to vibrations at lower frequencies. The more mobile unshared electrons of nitrogen are involved to a greater extent in conjugation. This explains the lower frequency of amides cf. esters. The lowest frequency is observed in the $-\text{CO}_2^-$ group.

In the series



possibilities of internal conjugation decrease in the order shown. The $-I$ effect of the atoms attached to the C=O group increases in the same order [2].

Table II-178 Characteristic frequencies of functional derivatives of carboxylic acids

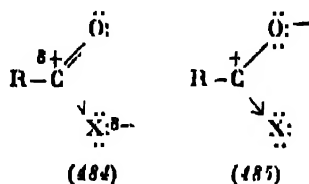
| Compound | Formula | Frequency, cm^{-1} |
|------------|--|-----------------------------|
| Halides | $\text{R}-\text{C} \begin{array}{l} \text{O} \\ \text{Hal} \end{array}$ | 1770–1870 |
| Esters | $\text{R}-\text{C} \begin{array}{l} \text{O} \\ \text{OR} \end{array}$ | 1735–1740 |
| Lactones | $\begin{array}{l} (\text{---C}_n\text{---})-\text{O} \\ \quad \\ \text{---C} \quad \text{CO} \\ \end{array} \begin{array}{l} n=1, \beta \\ n=2, \gamma \\ n=3, \delta \end{array}$ | 1818 1770 1740 |
| Anhydrides | $\text{R}-\text{C} \begin{array}{l} \text{O} \\ \text{O} \\ \text{R}-\text{C} \begin{array}{l} \text{O} \\ \text{O} \end{array} \end{array}$ | 1800–1825 |
| Peracids | $\text{R}-\text{C} \begin{array}{l} \text{O} \\ \text{O}-\text{OH} \end{array}$ | 830–890 |
| Peroxides | $\text{R}-\text{C} \begin{array}{l} \text{O} \\ \text{O}-\text{O}-\text{C}-\text{R} \\ \text{O} \end{array}$ | 1780–1820 1758–1793 |
| Amides | $\text{R}-\text{C} \begin{array}{l} \text{O} \\ \text{NH}_2 \end{array}$ | 1650–1715 |
| Nitriles | $\text{R}-\text{C}\equiv\text{N}$ | 2200–2260 |

Table II-178 shows the limits of νCO absorptions in functional derivatives described below. The table also included lactones (cyclic intramolecular esters of hydroxy acids).

A. ACID HALIDES

Acid halides are derivatives in which the OH group is replaced by a halogen atom.

The strong electronegativity of the halogen makes the carboxyl carbon more positive, favoring structure (484) over the polar structure (485). The $C=O$ frequency becomes characteristic by its very high value and differs from vibrations of other functional groups. In saturated carboxylic acid halides the ν_{CO} frequency lies in the range $1770\text{--}1876\text{ cm}^{-1}$ [3]. Within these



limits, it varies with the nature of the halogen and of the hydrocarbon group R. In the vapor phase, frequencies are $15\text{--}20\text{ cm}^{-1}$ higher than in the liquid phase [3].

Sometimes the infrared spectra show the presence of conformational isomers.

In the series $R-CO-X$, where $X=F, Cl, Br, I$, the increase in ν_{CO} frequency parallels that of the electronegativity of the halogen atom. The highest frequency is shown by fluorides and it decreases in the order $F > Cl > Br > I$.

Acetyl chloride in the vapor phase shows an absorption maximum at 1821 cm^{-1} along with two bands at 1815 and 1829 cm^{-1} [4]. In the liquid phase or in carbon tetrachloride solution, the frequency falls to 1806 cm^{-1} [5, 6]. In acid chlorides of the higher members of the series, the decrease in frequency due to the mass effect is very small. *n*-Octanoyl chloride absorbs at 1790 cm^{-1} [3] and phenylacetyl chloride at 1802 cm^{-1} [5]. The strong $-I$ effect of fluoride results in a large increase in frequency. Acetyl fluoride in the vapor phase absorbs at 1872 cm^{-1} [3].

In halides of α,β -unsaturated acids and aromatic acids, conjugation of the $C=O$ group with the $C=C$ bond or the aromatic ring results in a decrease in the $C=O$ bond order and, consequently, a decrease in its frequency. Benzoyl chloride has a strong band at 1773 cm^{-1} along with a weaker band at 1736 cm^{-1} [3, 5].

In halides of α -halogenated acids, the presence of the halogen atom adjacent to the $C=O$ group results in an increase in $\nu_{C=O}$ frequency, cf. unsubstituted analogs. The largest shift is due to fluorine (the most electronegative, with the most powerful $-I$ effect). The presence of three fluorine atoms in trifluoroacetyl fluoride (F_3C-COF) results in an increase in frequency to 1901 cm^{-1} (in the vapor phase), i. e. by 29 cm^{-1} cf. acetyl fluoride (1872 cm^{-1}) [7, 8].

The vibration is sensitive both to the inductive effect and the mass effect of the halogen atom.

In trifluoroacetyl halides, the decrease in frequency from fluoride to iodide is ca. 100 cm^{-1} (Table II-179).

Smaller shifts also occur in halides of bromo- and chloro-acids.

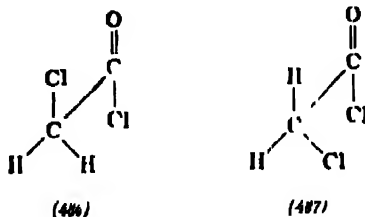
Spectra of mono- or disubstituted α -halogeno-acid halides show two νCO absorptions [6]. Doubling of the band occurs in the vapor phase, as well as in the liquid phase, or in solution. This behavior differentiates α -halogeno acid halides from α -halogenocarbonyl compounds which show a single band in the vapor phase [9]. The increased number of bands is due to conformational isomers (486) and (487).

Table II-178 νCO frequencies in trichloroacetyl halides

| Halide | νCO , cm^{-1} |
|----------------------------------|-----------------------------------|
| $\text{F}_3\text{C}-\text{COF}$ | 1901 |
| $\text{F}_3\text{C}-\text{COCl}$ | 1810 |
| $\text{F}_3\text{C}-\text{COBr}$ | 1838 |
| $\text{F}_3\text{C}-\text{COI}$ | 1812 |

Theory predicts that in the solid state the more stable isomer should have the more polar conformation (486), with chlorine and oxygen atoms *cis* to each other. This conformation should give rise to a band at a higher frequency than conformation (487). Assignments of bands in infrared spectra of monochloro- and monobromoacetic acids have been based on these considerations [10]. Table II-180 shows νCO frequencies of monochloro-, dichloro-, and trichloroacetyl chlorides in the vapor phase, in a nonpolar solvent, and in a polar solvent.

Under these conditions spectra of chloroacetyl- and dichloroacetyl chlorides show the two bands corresponding to conformations (486) and (487). Trichloroacetyl chloride has a single band as does acetyl chloride. The higher frequency band in monochloroacetyl chloride, corresponding to the more polar conformation (486), occurs at 1835 cm^{-1} (vapor), showing a shift of $+11\text{ cm}^{-1}$, cf. acetyl chloride. In dichloroacetyl chloride, the frequency decreases to 1823 cm^{-1} , being shifted only by $+2\text{ cm}^{-1}$ cf. acetyl chloride. In trichloroacetyl chloride the absorption at 1815 cm^{-1} is 6 cm^{-1} , lower than in acetyl chloride. The lower frequency band arising from the less polar conformation (487) also shows an abnormal behavior. In monochloroacetyl chloride the band frequency is 23 cm^{-1} lower than in acetyl chloride and in the dichloro compound, the decrease in frequency is still larger [6].



This abnormal behavior, cf. α -halogenated carbonyl compounds, was attributed to the field effect of the chlorine atom which in conformation (486) is *cis* to oxygen and in conformation (487) is rotated by 120° .

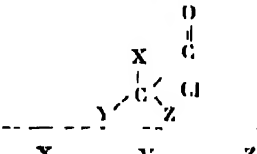
The increase in ν_{CO} frequency is due primarily to the $-I$ effect of the chlorine atom attached to the $\text{C}=\text{O}$ group (in acetone, where the chlorine atom is replaced by a methyl group with a $+I$ effect, the ν_{CO} frequency is

Table II-180 Characteristic frequencies in chlorides of chloroacetic acids

| Acid Chloride | Vapor | Frequency ν_{CO} , cm^{-1} | | | |
|-----------------------------|-----------|--|------|------------------------------------|------|
| | | Solution in CCl_4 | | Solution in CH_3CN | |
| $\text{CH}_3\text{-COCl}$ | 1821 | 1806 | | 1807 | |
| $\text{ClCH}_2\text{-COCl}$ | 1835 1798 | 1821 | 1785 | 1817 | 1786 |
| $\text{Cl}_2\text{CH-COCl}$ | 1823 1790 | 1810 | 1779 | 1805 | 1783 |
| $\text{Cl}_3\text{C-COCl}$ | 1815 | 1803 | | 1803 | |

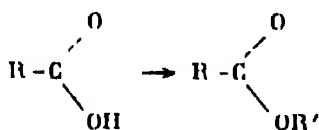
81 cm^{-1} lower than in acetyl chloride, CH_3COCl). The field effect of the two chlorine atoms diminishes the electronegativity of both atoms. This results in a decrease in ν_{CO} frequency. In conformation (486), the chlorine atom in the *cis* position adjacent to the oxygen atom repels the electrons of the CO group and its frequency increases by 14 cm^{-1} cf. versus acetyl chloride. In conformation (487) the chlorine atom rotated by 120° reduces the ν_{CO} frequency by the same number of cm^{-1} . Based on these observations, ν_{CO} frequencies have been calculated for various possible conformations of chlorides of mono-, di-, and trichloroacetic acids (Table II-181).

Table II-181 Calculated and experimental ν_{CO} frequencies in monochloro-, dichloro- and trichloroacetyl chlorides

| Compound |  | | | ν_{CO} calc. cm^{-1} | ν_{CO} exp. cm^{-1} |
|-----------------------------|--|----|----|---|--|
| | X | Y | Z | | |
| $\text{CH}_3\text{-COCl}$ | H | H | H | | 1821 |
| $\text{ClCH}_2\text{-COCl}$ | Cl | H | H | $1821 + 14 = 1835$ | 1835 |
| | H | Cl | H | $1821 - 14 = 1807$ | 1798 |
| $\text{Cl}_2\text{CH-COCl}$ | Cl | Cl | H | $1821 - 14 + 14 = 1821$ | 1823 |
| | H | Cl | Cl | $1821 - 28 = 1793$ | 1790 |
| $\text{Cl}_3\text{C-COCl}$ | Cl | Cl | Cl | $1821 + 14 - 28 = 1807$ | 1815 |

B. ESTERS OF CARBOXYLIC ACIDS

The functional group in esters formally results by replacing the hydrogen atom of the carboxyl group with an organic group R.



Consequently vibrations of $C=O$ and $C-O-R'$ bonds depend on the nature of R and mainly on the nature of R' .

As in the case of acids, the organic group R affects the electronic distribution in the $-COOR'$ group through its inductive and conjugative effects, causing a decrease in νCO frequency in unsaturated and aromatic compounds and an increase in frequency in derivatives substituted in the α -position with groups having a $-I$ effect (halogen, carbonyl, hydroxyl, etc.). Most characteristic, however, is the influence of the group R' . In the homologous series where $R' = \text{alkyl}$, the νCO frequency decreases (cf. to acids) because of the $+I$ effect of R' . If R' is an unsaturated or aromatic group capable of conjugation with the p electrons of oxygen, characteristic shifts in frequency are observed. In esters of aliphatic acids with phenols or unsaturated compounds, for example, the νCO frequency increases. In diaryl esters due to compensation of the two conjugative effects, the frequency has an intermediate value. It should be pointed out that any shift in $C=O$ frequency in one direction is compensated for by a shift in $-C-O-R'$ frequency in the opposite direction.

a. **CO stretching vibration.** 1. *Esters of saturated monocarboxylic acids with saturated alcohols.* Esters of saturated monocarboxylic acids have a constant νCO absorption between 1735 and 1740 cm^{-1} in the liquid phase [11] and $20-30\text{ cm}^{-1}$ higher (ca. 1765 cm^{-1}) in the vapor phase [4]. In solution the frequency varies with the nature of the solvent, lying in the range $1735-1756\text{ cm}^{-1}$. Esters of formic acid are an exception. In the liquid phase their mean frequency is 1723 cm^{-1} and in the vapor phase 1755 cm^{-1} [4]. Table II-182 shows mean frequencies of some esters $RCOOR'$ where $R = CH_3$, C_2H_5 , $n-C_3H_7$, $i-C_3H_7$, $n-C_4H_9$, $i-C_4H_9$, $i-C_5H_{11}$, and $R' = \text{alkyl}$, cycloalkyl.

Methyl, ethyl, and propyl acetates in the vapor phase have two distinct maxima, separated by $10-15\text{ cm}^{-1}$. They are attributed to envelopes of P and R branches of the rotational-vibrational spectra [12]. Chain lengthening of R' in the alcohol and of R in the acid does not affect the $\nu C=O$ frequency. Esters of higher aliphatic acids have the same frequencies as lower members of the series. Methyl stearate (in solution) absorbs at 1741 cm^{-1} [13, 14]. Neither does branching in the α -position affect the vibration. Esters of dimethyl- and trimethylacetic acids have normal frequencies (Table II-182).

Esters of cycloalkanecarboxylic acids with strain-free rings have νCO frequencies in the range $1735-1740\text{ cm}^{-1}$ [15]. Saturated esters in the steroid series have normal frequencies ($1735-1742\text{ cm}^{-1}$) [16, 17].

The intensity of νCO bands is characteristic for various classes of esters and varies considerably from one class to another [18-21]. In esters of satu-

Table II-182 Mean νCO frequencies in esters of saturated aliphatic acids*

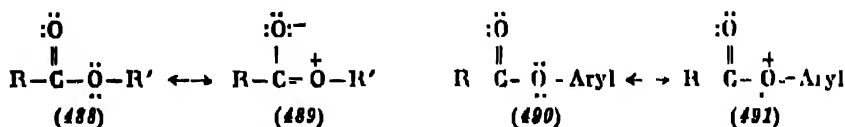
| Ester | $\nu CO, \text{cm}^{-1}$ |
|-----------------------------|--------------------------|
| $H-COOR'$ | 1752-1757 |
| CH_3-COOR' | 1762-1774 |
| CH_3CH_2-COOR' | 1758-1767 |
| $CH_3CH_2CH_2-COOR'$ | 1758-1760 |
| $(CH_3)_2CH-COOR'$ | 1757-1759 |
| $(CH_3)_2C-COOCCH_3$ | 1758 |
| $(CH_3)_2CH-CH_2-COOC_2H_5$ | 1759 |

* In the vapor phase.

rated acids with saturated alcohols, the molar extinction coefficient is 570–610 units. Frequencies and intensities of absorption enable the differentiation between various types of esters [20–23].

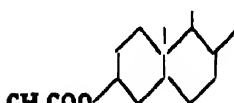
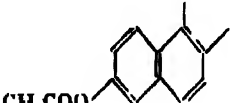
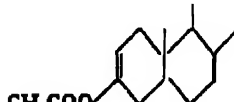
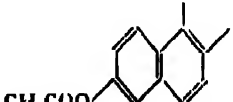
2. *Esters of saturated acids with phenols ($R' = \text{aryl}$)*. In esters of aliphatic acids with phenols, the νCO frequency increases substantially, cf. alkylesters. Phenyl acetate $\text{CH}_3\text{COOC}_6\text{H}_5$ absorbs at 1754 cm^{-1} [24] in carbon tetrachloride, at 1793 cm^{-1} in the vapor phase, and at 1766 cm^{-1} in the liquid state [4]. *p*-Nitrophenyl acetate [5] absorbs in solution at 1786 cm^{-1} . Shifts toward higher frequencies are due to the $-I$ and $-E$ effects of the NO_2 group in the *para* position of the benzene ring.

The general increase in frequency in these compounds is due to conjugation between the unshared electrons of the oxygen atom and the aromatic ring. This destroys the normal conjugation of the ester group (488) and (489), favoring structures (490) and (491).



The phenomenon has been pointed out fairly clearly with some steroid acetates with the OH group in saturated or unsaturated rings, or an aromatic ring (Table II-183) [25, 26].

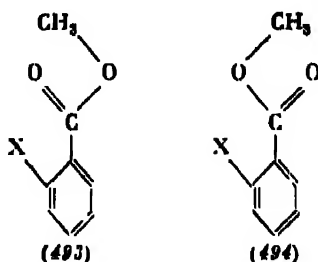
Table II-183 Characteristic frequencies of the COOR' group in some steroid esters [26]

| Ester | Frequency, cm^{-1} | | Ester | Frequency, cm^{-1} | |
|---|-----------------------------|---------------------------------|---|-----------------------------|---------------------------------|
| | $\nu\text{C}=\text{O}$ | $\nu\text{C}-\text{O}-\text{C}$ | | $\nu\text{C}=\text{O}$ | $\nu\text{C}-\text{O}-\text{C}$ |
|  | 1735 | 1239 |  | 1766 | 1204 |
|  | 1755 | 1217 |  | 1770 | 1204 |

Esters of saturated acids with unsaturated alcohols. The vibration of the $\text{C}=\text{O}$ group is affected only by the double bond in the immediate vicinity of the oxygen atom $\text{R}-\text{COOC}=\text{C}-$. In vinyl esters $\text{RCOOCH}=\text{CH}_2$, the frequency is very high [4, 24]. Vinyl acetate absorbs at 1776 cm^{-1} in carbon tetrachloride solution [24], at 1787 cm^{-1} in the vapor phase, and at 1770 cm^{-1} in the liquid state [4, 5].

Alkyl acetate $\text{CH}_3\text{COOCH}_2-\text{CH}=\text{CH}_2$ has an almost normal absorption at 1768 cm^{-1} in the vapor phase, and at 1745 cm^{-1} in carbon tetrachloride solution [12].

Band doubling in *ortho*-substituted compounds is due to isomers (493) and (494).



The higher frequency band (1740 cm^{-1}) is assigned to structure (494), where the CO group is opposite to X and the lower frequency band is assigned to structure (493) where vectors C=O and C-X have the same orientation [31].

5. *Esters of aromatic acids with phenols.* The νCO frequency in diaryl esters is 1746 cm^{-1} [26]. It is intermediate between frequencies of esters of aromatic acids with saturated alcohols, $\text{Ar}-\text{COOR}'$ (1720 cm^{-1}) and esters of aliphatic acids with phenols, $\text{R}-\text{COOAr}$ (1766 cm^{-1}). This is due to competition of the two aromatic rings for conjugation with the unshared electrons of the ester oxygen [26].

6. *Esters of unsaturated acids with double bonds.* The effect of the double bond on the $-\text{COOR}'$ vibration depends on its position relative to this group.

Esters of α,β -unsaturated acids with the double bond adjacent to the COOR group have lower νCO frequencies than saturated esters. The mean value of the frequency is 1720 cm^{-1} [4, 11, 32–35]. Characteristic frequencies of some α,β -unsaturated esters are shown in Table II-186.

Table II-186 Characteristic frequencies (cm^{-1}) in α,β -unsaturated esters [3,4]

| Ester | C=C Isomer | νCO (in CS_2) | $\nu\text{C}=\text{C}$ (in CCl_4) | Out-of-plane CH de- formation (in CS_2) | |
|---|--------------------|---------------------------------------|--|--|-----|
| | | | | Trans | Cis |
| $\text{CH}_2=\text{CH}-\text{COOCH}_3$ | | 1718 | | | |
| $\text{CH}_3-\text{CH}=\text{CH}-\text{COOCH}_3$ | <i>trans</i> | 1726 | 1659 | 969 | |
| $\text{CH}_3-\text{CH}=\text{CH}-\text{COOCH}_3$ | <i>cis</i> | 1721 | 1644 | — | 812 |
| $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{COOCH}_3$ | <i>trans-trans</i> | 1716 | 1642 1614 | 995, 943 | — |
| $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{COOCH}_3$ | <i>cis-trans</i> | 1715 | 1634 1598 | 990, 951, 936 | — |
| $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{COOCH}_3$ | <i>trans-cis</i> | 1715 | 1639 1597 | 996, 958, 938 | 832 |
| $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{COOCH}_3$ | <i>cis-cis</i> | 1715 | 1623 1587 | — | 821 |
| $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-\text{COOCH}_3$ | <i>trans</i> | 1719 | 1615 | 959 | — |
| $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}=\text{CH}-\text{COOCH}_3$ | <i>cis</i> | 1733 | 1612 | — | 812 |
| | | 1718 | | | |

The decrease in frequency is attributed to conjugation of the COOR' group with the α,β -double bond.

Extension of the conjugated double bond system results in an insignificant decrease in frequency, cf. that determined by the α,β -double bond.

The intensity of the νCO band does not vary very much with the nature of the unsaturated system.

In conjugated α,β -unsaturated esters, the $-\text{COOR}'$ is coplanar with the $\text{C}=\text{C}$ double bond. The molecules can adopt either the *s-cis* or the *s-trans* configuration. Because of this some esters show two νCO absorptions [36].

7. *Esters of unsaturated acids with triple bonds.* In conjugated α,β -unsaturated esters with triple bonds, the νCO frequency decreases to ca. 1717 cm^{-1} . On extension of the triple bond system, a slight increase in frequency is observed cf. unsaturated esters with double bonds. Characteristic frequencies of some acetylenic esters are shown in Table II-187 [33].

Table II-187 Characteristic frequencies of acetylenic esters [33]

| Ester | Frequency, cm^{-1} | | |
|--|---|---------------------------------------|---|
| | $\nu\text{C}\equiv\text{C}$ (in CCl_4) | νCO (in CS_2) | $\nu\text{C}-\text{C}-\text{COOR}$ (in CS_2) |
| $\text{HC}\equiv\text{C}-\text{COOCH}_3$ | | 1719 | 750 |
| $\text{CH}_3-\text{C}\equiv\text{C}-\text{COOCH}_3$ | 2212 | 1718 | 748 |
| $\text{CH}_3-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{COOCH}_3$ | 2260 2190 | 1716 | 740 |
| $\text{CH}_3-(\text{C}\equiv\text{C})_2-\text{COOCH}_3$ | 2210 2125 | 1721 | 740 |

8. *Esters of dicarboxylic acids.* The normal νCO frequency in esters of dicarboxylic acids is 1740 cm^{-1} [5, 18, 37, 38]. In malonic ester, where the two carboalkoxy groups are attached to the same carbon atom, the band is split due to either coupling of the symmetrical and asymmetrical vibrations or to resonance coupling with an overtone. The two bands occur in the infrared spectrum at 1740 and 1757 cm^{-1} [38].

Starting with ω -dicarboxylic acids with four carbon atoms, a single $\nu\text{C}=\text{O}$ absorption occurs. Diethyl succinic ester absorbs at 1743 cm^{-1} and diethyl adipic ester at 1738 cm^{-1} (Table II-188).

Table II-188 νCO frequencies (cm^{-1}) in esters of saturated dicarboxylic acids [37]

| Ester | Dimethyl | | | Diethyl | | |
|--------------------|------------|------------|-------------|------------|------------|-------------|
| | Cryst. | Liquid | $\Delta\nu$ | Cryst. | Liquid | $\Delta\nu$ |
| Oxalic | | | | | 1754, 1744 | — |
| Malonic | | 1750, 1768 | | | 1750, 1764 | |
| Succinic | 1742 | 1751 | +9 | 1743 | 1753 | +10 |
| Glutaric | 1740 | 1749 | +9 | 1730 | 1741 | +11 |
| Adipic | 1754 | 1752 | -2 | 1738 | 1749 | +11 |
| Pimelic | 1740(1741) | 1749 | +9 | 1738(1744) | 1739 | +1 |
| Suberic | 1751 | 1740 | -2 | 1713 | 1741 | -2 |
| Acelaic | 1745 | 1743 | -2 | 1750 | 1745 | -5 |
| Sebacic | 1750 | 1755 | +5 | 1740 | 1747 | +7 |
| Decanedicarboxylic | 1753 | 1753 | 0 | 1745 | 1733 | +12 |

No large differences in frequency are observed between spectra recorded in the liquid or solid state [37].

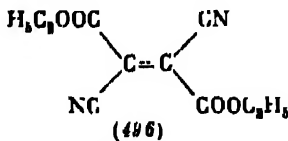
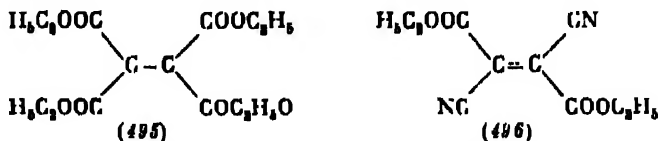
In dimethylesters νCO frequencies are higher in even-numbered than in odd-numbered members (oxalic acid is an exception). The behavior is similar to that observed in monocarboxylic acids (1705 cm^{-1} in C_{12} , C_{14} , C_{16} , etc. and $1698\text{--}1701\text{ cm}^{-1}$ in C_{11} , C_{13} , C_{15} , etc.) [14].

νCO frequencies of methyl and ethyl esters of saturated dicarboxylic acids are shown in Table II-188 [37].

The mean νCO frequency in even-numbered methyl esters ($n \geq 4$) in the crystalline state is $1750\text{--}1754\text{ cm}^{-1}$ and in the liquid state, $1749\text{--}1755\text{ cm}^{-1}$. Odd-numbered esters ($n \geq 3$) absorb at $1740\text{--}1745\text{ cm}^{-1}$ in the crystalline state and at $1743\text{--}1749\text{ cm}^{-1}$ in the liquid state.

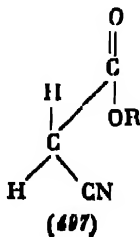
In ethyl esters the limits are larger: $1738\text{--}1750\text{ cm}^{-1}$ (crystalline, even-numbered), $1733\text{--}1753\text{ cm}^{-1}$ (liquid, even-numbered), $1730\text{--}1750\text{ cm}^{-1}$ (crystalline, odd-numbered), and $1739\text{--}1745\text{ cm}^{-1}$ (liquid, odd-numbered) [37].

In esters of unsaturated acids with carboxyl groups directly attached to the double bond, the νCO frequency increases ca. 5 cm^{-1} cf. monocarboxylic α,β -unsaturated esters. Fumaric ester absorbs at 1727 cm^{-1} , (in CCl_4), and maleic ester has a slightly higher frequency (1734 cm^{-1}). The higher frequency in maleic ester is attributed to the disappearance of conjugation as a result of a twisting of the COOR group out of the plane of the $\text{C}=\text{C}$ bond. This deviation from coplanarity is due to a secondary steric effect [39]. In this case the frequency is close to that in nonconjugated compounds. The same effect is also observed in other compounds. The spectrum of tetracarbethoxyethylene (495) shows two bands, 1739 and 1750 cm^{-1} (in CCl_4), with frequencies very close to those of the saturated analog tetracarbethoxyethane, absorbing at 1742 and 1751 cm^{-1} .



In 1,2-dicyano-1, 2-dicarbethoxyethylene (496), only the frequency of the CN group decreases. The νCO frequency has the normal value of saturated esters. It is assumed that only the CN group coplanar with $\text{C}=\text{C}$ is conjugated with the double bond, whereas the COOR' groups are out-of-plane [38].

In cyanoacetic ester $\text{NC}-\text{CH}_2-\text{COOR}$, the νCO frequency is 1756 cm^{-1} in nonpolar solvents (CCl_4) and 1750 cm^{-1} in acetonitrile [10]. By analogy with α -halogenated esters, the increase in frequency is attributed to the $-I$ effect of the $\text{C}\equiv\text{N}$ group. It is assumed that cyanoacetic ester has a staggered *syn* conformation (497).



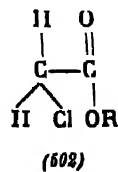
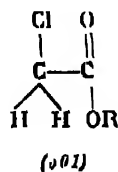
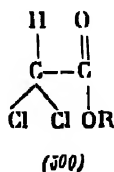
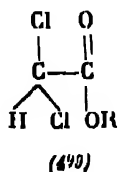
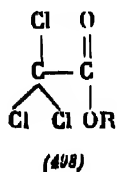
9. *Esters of α -halogenated acids.* The presence of an electronegative halogen atom in the α -position with respect to the COOR' group results in an increase in $\nu\text{C}=\text{O}$ frequency, cf. unsubstituted esters. The highest frequency is observed in fluoroesters. It decreases with the electronegativity of the halogen atom. In trichloroacetic ester, the frequency is 1770 cm^{-1} and in trifluoroacetic ester, 1789 cm^{-1} , cf. 1740 cm^{-1} in methyl acetate (carbon tetrachloride solution or liquid) (Table II-189) [4, 8, 12, 41]. The increase in frequency is due to the $-I$ effect and to the field effect of the halogen atom on the readily polarizable oxygen atom [8] (see Carbonyl compounds and α -halogenated acids).

Table II-189 Characteristic frequencies in α -halogenated ethylacetates (liquid film) [41]

| Ester (R=C) | Frequency, cm^{-1} | | | |
|------------------------------------|-----------------------------|------------------------|-------------------------|-------------------------|
| | $\nu\text{C}=\text{O}$ | $\nu\text{C}-\text{O}$ | $\nu\text{C}-\text{Cl}$ | $\nu\text{C}-\text{Br}$ |
| CH_3-COOR | 1740 | 1236 1215 | — | — |
| $\text{CH}_2\text{Br}-\text{COOR}$ | 1740 | 1281 | — | 553 |
| $\text{CHBr}_2-\text{COOR}$ | 1753 1730 | 1268 1278 | — | 583 598 large |
| $\text{CH}_2\text{Cl}-\text{COOR}$ | 1753 | 1288 1311 | 697 | — |
| $\text{CHBrF}-\text{COOR}$ | 1754 | 1284 | — | 594 |
| $\text{CHClF}-\text{COOR}$ | 1754 | 1276 1290 | 731 | — |
| $\text{CHCl}_2-\text{COOR}$ | 1758 | 1268 1302 | 719 | — |
| $\text{CHBrCl}-\text{COOR}$ | 1758 1742 | 1265 1266 | — | — |
| CCl_3-COOR | 1770 | 1310 1266 | — | — |
| CHF_2-COOR | 1778 1750 | 1290* | — | — |
| CHF_3-COOR | 1770 | — | — | — |
| CF_3-COOR | 1789 | — | — | — |

* Only one band is observed instead of two because of recording in liquid film where the less polar form disappears [2].

Comparative studies of mono-, di-, and trihalogenated methyl and ethyl acetates in the gaseous phase, liquid state, or in solution have shown that some of them have two νCO bands and others only one. Splitting of the νCO band in compounds with a halogen atom in the α -position was attributed to the presence of conformational isomers [8, 12, 42]. In the vapor phase trichloroacetic ester, with three identical atoms at the α -carbon, shows a single band at 1784 cm^{-1} . In carbon tetrachloride solution or in the liquid state this band occurs at 1770 cm^{-1} [12, 41]. In this compound (498) one chlorine atom has to be *cis* to the CO group, whereas the other two are twisted by 120° and have equivalent electrostatic positions [12].



Spectra of difluoro-, dichloro-, and dibromoacetic esters show two bands 18–25 cm^{-1} apart, both in the vapor phase and in solution [18, 12, 40, 41, 43]. This splitting was attributed to the presence of conformational isomers (499) and (500) in equilibrium [8, 12, 40, 43]. The higher frequency corresponds to the more polar conformation (499) with a chlorine atom *cis* to oxygen and the lower frequency, to conformation (500) [8]. The distance between the two bands seems to be temperature independent; however, the intensity of the higher frequency absorption decreases in the vapor phase [12]. The frequency of conformation (499) is close to that in trichloroacetic ester, whereas the low frequency coincides with that in methyl or ethyl acetate (Table II-190).

Table II-190 νCO frequencies in α -halogenated esters [12]

| Ester | $\nu\text{CO}, \text{cm}^{-1}$ | |
|---|--------------------------------|----------------------------|
| | Vapor | Solution in CCl_4 |
| Methyl ester | | |
| $\text{CH}_3-\text{COOCH}_3$ | 1771 | 1719 |
| $\text{CH}_2\text{Cl}-\text{COOCH}_3$ | 1771 | 1749 1773 |
| $\text{CHCl}_2-\text{COOCH}_3$ | 1771 1798 | 1755 1775 |
| $\text{CCl}_3-\text{COOCH}_3$ | 1790 | 1775 |
| $\text{CH}_2\text{Br}-\text{COOCH}_3$ | 1770 | 1719 1761 |
| Ethyl ester | | |
| $\text{CH}_3\text{CH}_2-\text{COOC}_2\text{H}_5$ | 1765 | 1743 |
| $\text{CHClCH}_2-\text{COOC}_2\text{H}_5$ | 1766 | 1742 1767 |
| $\text{CCl}_2\text{CH}_2-\text{COOC}_2\text{H}_5$ | 1781 | 1770 |
| $\text{CH}_2\text{Br}-\text{COOC}_2\text{H}_5$ | 1763 | 1743 1761 |
| $\text{CHBr}_2-\text{COOC}_2\text{H}_5$ | 1757 1780 | 1742 1761 |
| Allyl ester | | |
| $\text{CH}_2=\text{CH}-\text{COOCH}_2\text{CH}=\text{CH}_2$ | 1768 | 1745 |
| $\text{CHCl}-\text{CH}=\text{CH}-\text{COOCH}_2\text{CH}=\text{CH}_2$ | 1765 | 1746 1768 |
| $\text{CHCl}_2-\text{CH}=\text{CH}-\text{COOCH}_2\text{CH}=\text{CH}_2$ | 1763 1786 | 1752 1772 |
| $\text{CCl}_3-\text{CH}=\text{CH}-\text{COOCH}_2\text{CH}=\text{CH}_2$ | 1784 | 1770 |

Methyl or ethyl monochloro- and monobromoacetates in the vapor phase [12] or in the liquid state [41] show a single band at 1771 and 1770 cm^{-1} , respectively, in the νCO region. In carbon tetrachloride solution, two bands occur: 1749 and 1773 cm^{-1} in methyl monochloroacetate [8, 12, 40] and 1749 and 1761 cm^{-1} in methylbromoacetate [12]. In some papers the lower frequency band was not reported in spectra recorded in the vapor or liquid phase. It is believed that under these conditions one of the isomers either disappears completely or is present in a very low concentration. Here, too, the higher frequency absorption is assigned to conformation (501) and the lower, to conformation (502).

Band intensity studies in various solvents [10] and at various temperatures [43] give some indications regarding the contribution of the steric factor and the inductive effect to isomer distribution at equilibrium. The $-I$ effect does not affect the intensity but determines the frequency of the absorption [8, 12].

The *ortho*-halogenobenzoic esters [31, 44–46] show two νCO absorptions assigned to conformational isomers (503) and (504). The intensity of the higher frequency band increases in acetonitrile (more polar solvent) (Table II-191).

Table II-191 νCO frequencies (cm^{-1}) in *O*-substituted methyl benzoates [31]

| Substituent | CCl_4 | | <i>n</i> -Hexane | | CH_3CN | |
|---------------------------|----------------|------------|------------------|------------|------------------------|------------|
| | νCO | ϵ | νCO | ϵ | νCO | ϵ |
| <i>o</i> -CH ₃ | 1736 | 430 | 1745 | 395 | 1731 | 505 |
| <i>o</i> -F | 1718 | 265 | 1723 | 305 | (1709)* | 105 |
| | 1741 | 315 | 1749 | 260 | 1733 | 520 |
| | 1726 | 510 | 1731 | 425 | 1723 | 425 |
| <i>o</i> -Cl | 1744 | 410 | 1750 | 465 | 1736 | 480 |
| | 1727 | 240 | 1733 | 285 | 1724* | (120) |
| <i>o</i> -Br | 1744 | 465 | 1750 | 550 | 1737 | 535 |
| | 1727 | (195) | 1735 | 240 | 1729 | (135) |
| <i>o</i> -I | 1740 | 550 | 1746 | 630 | 1733 | 540 |
| | 1727* | (160) | 1736* | (200) | 1725 | (85) |
| <i>o</i> -NO ₂ | 1747 | 710 | | | | |
| | 1730 | 900 | 1735 | 1035 | 1724 | 790 |

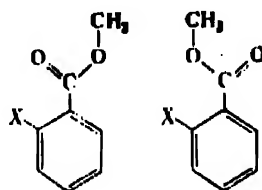
* Shoulder; estimated values are given in parenthesis.

By analogy with aliphatic α -halogenated esters, the higher frequency band was assigned to the more polar form (503) where the vectors of the $\text{C}=\text{O}$ and $\text{C}-\text{X}$ dipoles are parallel. The other absorption belongs to conformation (504).

10. *Esters of hydroxyacids.* In esters of salicylic acids, the $\text{C}=\text{O}$ group forms intramolecular (chelate) hydrogen bonds with the phenolic hydroxyl and the frequency decreases to 1684 cm^{-1} . The shift, cf. methyl benzoate (1730 cm^{-1}), is -46 cm^{-1} [28]. Alkyl substituents in the ring in positions which do not interfere with the chelate system do not alter the frequency. Substituents in the 3- and 6- positions

Table II-192 νCO and νOH frequencies (cm^{-1}) in methyl esters of substituted salicylic acids

| Substituent | νCO (CCl_4) | Bonded νOH (in CCl_4) |
|-------------------------------|--------------------------------------|---|
| 4-Methyl | 1681 | 3200 |
| 3-Methyl | 1681 | 3195 |
| 3- <i>t</i> -Butyl | 1676 | (3110) |
| 6-Methyl | 1671 | 3120 |
| 3-Isopropyl-6-methyl | 1663 | (3040) |
| Methyl salicylate | 1684 | 3210 |
| <i>tert</i> -Butyl salicylate | 1674 | 3180 |



(503)

(504)

reduce the frequency. The shift depends on the size of the substituent. Unsubstituted methyl and *t*-butyl esters are listed in Table II-192 for comparison.

A similar *ortho* effect is observed in other esters of aromatic *o*-hydroxyacids with substituents adjacent to the chelate group. The ester of 9-hydroxy-

phenanthrene-10-carboxylic acid absorbs at 1649 cm^{-1} . This frequency is much lower than in normal (nonchelated) aromatic structures [29, 47].

Esters of α,β -unsaturated β -hydroxyacids are enolic forms of β -ketoesters, which also have chelate structures (see below).

b. **Other characteristic frequencies in esters.** Spectra of esters show a strong band in the range $1150\text{--}1280\text{ cm}^{-1}$ [1, 48, 49], accompanied by one or several bands of variable intensity between 1000 and 1300 cm^{-1} . These bands have been associated with various modes of coupled C—O and O—R' vibrations of the COOR' group [11, 50].

Table II-193 $\nu\text{C—O}$ frequencies in esters of carboxylic acids [49]

| Ester, R' = alkyl, steroid | $\nu\text{CO}, \text{cm}^{-1}$ |
|--|--------------------------------|
| H—COOH' | 1175—1185* |
| R—COOH' (R = C_2H_5 , C_3H_7 , etc.) | 1185—1190 |
| $(\text{CH}_2)_n\text{CH—COOR'}$ | 1200 |
| $\text{CH}_2\text{—COOR'}$ | 1232—1257 |
| $\text{C}_6\text{H}_5\text{—COOR'}$ | 1270 |
| $\text{CH}_2\text{—COOCH=CHR}$ | 1098—1159 |
| R—COOCH ₃ | 1155—1173 |
| $\text{HalCH}_2\text{—COOC}_2\text{H}_5$ | 1260—1310 |
| $\text{Hal}_2\text{CH—COOC}_2\text{H}_5$ | 1265—1278 |

[50], $1150\text{--}1220\text{ cm}^{-1}$

In acetates the strong 1240 cm^{-1} is frequently split. This splitting was attributed to the presence of several conformational isomers [48, 50, 51].

Table II-193 shows the regions containing characteristic C—O frequencies in various types of esters [49].

Studies of band positions and intensities in this region reveal some

particularities useful for identification purposes [50].

Methyl formate has a pair of bands (labeled *a* and *b* in Table II-194) between ca. 1150 and 1220 cm^{-1} . The two components shift together on chain lengthening. In general the lower frequency band is weaker and the relative intensity of both bands decreases along the series. Acetates seem to have a single band, but a more careful examination reveals two components. The higher frequency band is very weak in methyl acetate, but it becomes stronger in higher members. In methylpropionate the splitting is readily noticeable, whereas methyl butyrate and isobutyrate show more than two bands.

Table II-194 Frequencies and absolute intensities* of some alkyl esters [50]

| Ester | ν_a | | ν_b | | Total $A \cdot 10^3$ |
|----------------|------------------|----------------|------------------|----------------|-------------------------|
| | cm^{-1} | $A \cdot 10^3$ | cm^{-1} | $A \cdot 10^3$ | |
| Methyl formate | 1161 | 54.3 | 1214 | 9.25 | 147 |
| Ethyl formate | 1155 | 30.5 | 1195 | 14.00 | 170 |
| Butyl formate | 1151 | 14.4 | 1186 | 16.20 | 176 |
| Methyl acetate | 1253 | 133.0 | 1288 | 1.06 | 144 |
| Ethyl acetate | 1249 | (147) | 1273 | (19) | 166 |
| Amyl acetate | 1246 | (76.5) | 1260 | (86) | 163 |

A is expressed in $\text{cm} \cdot \text{mole}^{-1} \cdot \text{s}^{-1}$.

Since solvents with different association capability affect the band intensity differently in this region, it was assumed that the carbonyl group is involved in these vibrations. Table II-194 shows frequencies and absolute intensities of a number of alkyl esters in acetonitrile solution [50].

Methyl esters show three bands between 1350 and 1500 cm^{-1} : a strong one at 1436—1438 cm^{-1} and two weak ones at 1420—1427 and 1360—1362 cm^{-1} [49]. The 1436—1438 cm^{-1} band vanishes on deuteration. It was assigned to the δCH_3 vibration of the ester group COOCH_3 . The 1420 cm^{-1} band was assigned to the scissoring vibration of the CH_2 group adjacent to COOCH_3 . The 1378 cm^{-1} band probably belongs to the terminal CH_3 of the alkane chain of the acid.

Lactones

Lactones are intramolecular esters of hydroxyacids. Consequently, they show characteristic absorption of esters. The νCO frequency shift, cf. values in saturated esters, depends on ring size [52--55]. Table II-195 shows differences ($\Delta\nu\text{CO}$) between νCO frequencies in four- to seven-membered ring lactones along with νCO frequencies of saturated aliphatic esters.

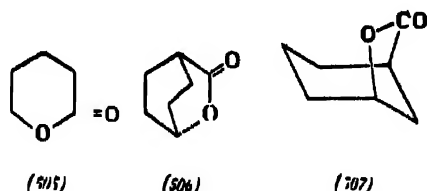
Table II-195 Effect of ring size on νCO frequencies in lactones [53, 54]

| No of ring carbons | 4 | 5 | 6 | 7 | Saturated aliphatic esters |
|-----------------------------------|------|------|------|------|----------------------------|
| Mean frequency | 1818 | 1770 | 1740 | 1727 | 1735 |
| $\Delta\nu$ in monocyclic lactone | + 83 | + 40 | + 5 | + 8 | — |
| $\Delta\nu$ in bicyclic lactone | — | + 29 | + 4 | — | — |

The higher νCO frequency in four- and five-membered rings is assumed to be due to changes in hybridization of the carbon atom in the $\text{C}=\text{O}$ group [53]. In six-membered ring lactones the frequency is almost normal. In smaller rings, the same as in carbocyclic analogs (see small rings), the carbon-oxygen bond has stronger s -character. This results in an increase in force constant, hence in frequency. The fall in frequency in the seven-membered ring can be associated with the decrease in $\text{C}=\text{O}$ bond order due to the same effect [53, 56].

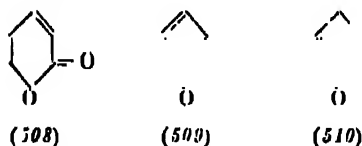
a. δ -Lactones. The vibration of the $\text{C}=\text{O}$ group in saturated δ -lactones has the same frequencies as in saturated aliphatic esters [54, 57]. The mean value is 1733—1739 cm^{-1} [57]. For example, δ -valerolactone absorbs at 1740 cm^{-1} (505) (in CCl_4) [53]. In polycyclic steroidal lactones, frequencies lie in the range 1737—1747 cm^{-1} [58]. In bridged bicyclic systems the value of the $\nu\text{C}=\text{O}$ frequency corresponds to that of the smallest ring. Bicyclic [2.2.2] lactones show frequencies of δ -lactones corresponding to a six-membered ring; 2-oxabicyclo [2.2.2] octanone-3 (506) absorbs at 1739 cm^{-1} [53].

Oxabicyclo [3.2.1] octanones, for example (507), have a five- and a seven-membered ring. The νCO frequency corresponds to the five-membered γ -lactonic ring.



In a series of strained steroidal spiro lactones frequencies lie in the range $1786-1793\text{ cm}^{-1}$ [48].

In unsaturated δ -lactones the νCO frequency depends on the position of the double bond relative to the C - O group [59]. In α,β -unsaturated lactones (508), the frequency decreases to $1708-1710\text{ cm}^{-1}$ (sometimes the band is split; see γ -lactones). The frequency becomes normal in nonconjugated compounds (509), absorbing between 1725 and 1740 cm^{-1} . A double bond in the vicinity of the alcoholic oxygen raises the frequency (the same as in vinyl alcohols). Lactones (510) absorb at $1770-1775\text{ cm}^{-1}$.

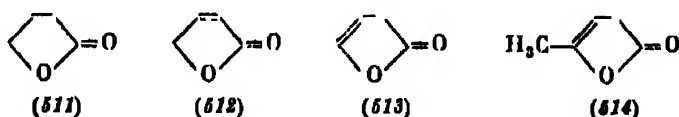


The νCO frequency in coumarin is $1695-1710\text{ cm}^{-1}$ in chloroform [60] and 1730 cm^{-1} in nujol [61]. The same frequency occurs in 4-hydroxycoumarin. In 3-substituted hydroxycoumarins the frequency is shifted to $1704-1730\text{ cm}^{-1}$ [62, 63].

Other characteristic vibrations in δ -lactones. Deformation vibrations of the CH_2 group in the position relative to oxygen absorb at 1400 cm^{-1} [58]. The frequency of the $\nu\text{C}-\text{O}$ vibration occurs at $1220-1240\text{ cm}^{-1}$ [57]. Deformation vibration of the CH_2 group in the α -position relative to the $\text{C}=\text{O}$ group give rise to absorptions between 1118 and 1422 cm^{-1} .

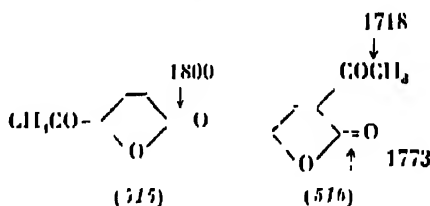
b. γ -Lactones. νCO frequencies in saturated γ -lactones are $35-40\text{ cm}^{-1}$ higher than in δ -lactones [52, 53, 54]. The reason for this rise in frequency was given above. γ -Butyrolactone (511) absorbs at 1775 cm^{-1} (in CCl_4) [5, 53]. The frequency does not vary much with the nature of the solvent or the physical state of the sample. γ -Lactones absorb at $1775-1790\text{ cm}^{-1}$ in carbon tetrachloride, at $1770-1785\text{ cm}^{-1}$ in chloroform, and at 1770 cm^{-1} in the solid state [58]. In α,β -unsaturated γ -lactones (512) (and in some α,β -unsaturated δ -lactones), the νCO band is split into two components of unequal intensities with frequencies of 1785 and 1755 cm^{-1} (in CS_2). The relative intensity of the two bands varies with solvent polarity and with temperature [64]. The lower frequency band (1755 cm^{-1}) is assigned to the normal νCO vibration [58]. The second band was assigned

to a Fermi resonance with an overtone [65]. The intensity of the higher frequency band decreases with increasing solvent polarity [51].

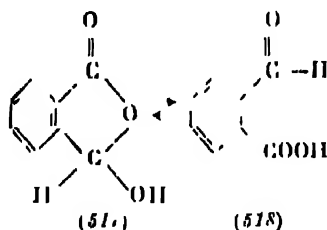


The $\nu_{C=C}$ absorption in these lactones occurs at $1620\text{--}1630\text{ cm}^{-1}$ [58].

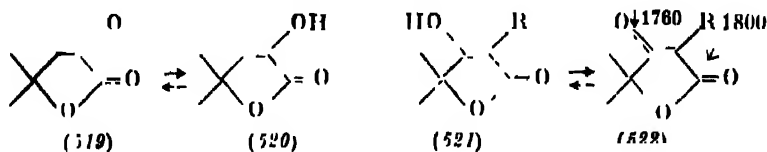
In β , γ -unsaturated γ -lactones (513) [5, 32, 65] the ν_{CO} frequency is 1800 cm^{-1} (corresponding to enol-lactones [66]). α -Angelica-lactone (514) absorbs at 1799 cm^{-1} [66]. γ -Lactones substituted with electronegative groups in the α -position also have higher $\nu_{C=O}$ frequencies (1800 cm^{-1}). The $-I$ effect of the $C=O$ group adjacent to oxygen can be demonstrated by comparing the two isomeric acetyl-butyrolactones (515) and (516). The ν_{CO} frequency in the lactonic ring is 1800 cm^{-1} in (515) and 1773 cm^{-1} in (516). The CO group of the acetyl group absorbs at 1718 cm^{-1} [5].



In phthalides (517) [67, 68] the ν_{CO} frequency lies in the range $1750\text{--}1780\text{ cm}^{-1}$. Infrared spectra have been used in many instances to establish the tautomerism (517) \rightleftharpoons (518) [67, 69].



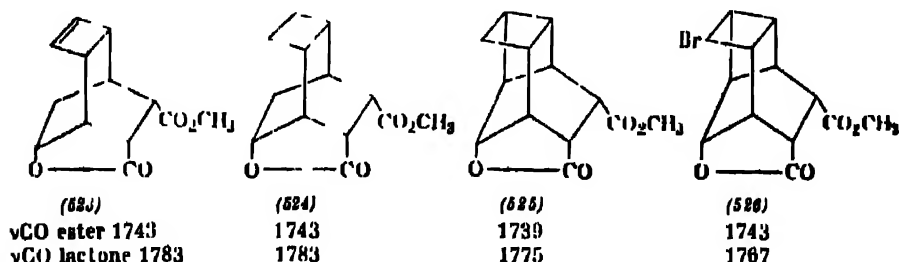
In lactones of γ -hydroxy- α -ketoacids (α -keto- γ -lactones) [70] of structure (519) the enolic form shows the following absorptions: $\nu_{CO}=1760\text{ cm}^{-1}$, $\nu_{OH}=3510\text{ cm}^{-1}$ and $\nu_{C=C}=1700\text{ cm}^{-1}$.



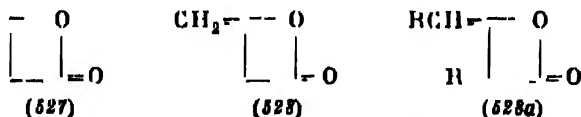
In the spectrum of treonic acid, absorptions arising from both tautomeric forms (521) and (522) can be identified [51]. In the keto-form (522),

the frequency of the lactonic CO group is 1800 cm^{-1} and that of the β -keto group is 1760 cm^{-1} (solution in CH_2Cl_2). The enolic form (521) has the νCO frequency at $1740\text{--}1750\text{ cm}^{-1}$ in compounds where R is not hydrogen. $\nu\text{C}=\text{C}$ occurs at 1675 cm^{-1} when R = alkyl and at 1630 cm^{-1} when R = H. The νOH absorption gives rise to a broad band centered at $2800\text{--}2900\text{ cm}^{-1}$ (chelate hydroxyl) [71].

In lactones (523)–(526) absorptions arising from both the lactonic and the ester CO groups can be observed [72].



c. β -Lactones. The νCO frequency in β -lactones is ca. 100 cm^{-1} higher than that in acyclic esters or in δ -lactones. This large shift is attributed to change in hybridization due to the strained four-membered ring. β -Propiolactone (527) absorbs at 1841 cm^{-1} in carbon tetrachloride solution and at 1834 cm^{-1} in methanol [53]. $\Delta\nu\text{CO}$ of only 7 cm^{-1} shows that the tendency toward hydrogen bonding is smaller in β -lactones than in γ -lactones ($\Delta\nu\text{CO } 12\text{ cm}^{-1}$) or in δ -lactones ($\Delta\nu\text{CO} = 15\text{ cm}^{-1}$) [73].



In ketene dimer (528) the νCO frequency is higher. The spectrum shows two bands: 1900 and 1867 cm^{-1} (in CCl_4). The unusually high frequency band at 1708 cm^{-1} is assigned to the exocyclic double bond [74, 75]. Aldoketene dimers with lactonic structure (528a) show bands at 1910 , 1857 , and 1710 cm^{-1} [75a].

C. ANHYDRIDES

Carboxylic acid anhydrides are characterized by a doublet in the $1750\text{--}1850\text{ cm}^{-1}$ region because of coupled vibrations of the two CO groups [76–78]. The higher frequency band is assigned to the symmetric vibration and the lower frequency band to the asymmetric vibration [78, 79]. Table II-196 shows νCO frequencies for some characteristic anhydrides [78].

In acyclic anhydrides of saturated carboxylic acids the two bands ($1800\text{--}1825$ and $1740\text{--}1760\text{ cm}^{-1}$) are almost of equal intensity (the ratio of optical densities is $0.8\text{--}0.9$) (see Table II-196).

Table 11-198 ν CO frequencies in anhydrides, cm^{-1} [78]

| Anhydride | Vibration | | | | Ratio $\frac{\text{O.D. asym}}{\text{O.D. sym}}$ |
|------------------------------------|----------------|-------------|---------------|--------------|---|
| | ν CO sym | O.D. sym** | ν CO asym | O.D. asym*** | |
| | 1825 | 0.150 | 1754 | 0.140 | 0.92 |
| $(\text{R}-\text{CO})_2\text{O}^*$ | 1800-1825 | 0.150-0.190 | 1740-1760 | 0.140-0.150 | 0.91-0.9 |
| | 1812 | 0.065 | 1764 | 0.170 | 2.7 |
| | 1806 | 0.054 | 1792 | 0.367 | 6.8 |
| | 1859 | 0.042 | 1786 | 0.264 | 6.3 |
| | 1855 | 0.048 | 1783 | 0.362 | 7.6 |
| | 1862 | 0.048 | 1799 | 0.402 | 8.4 |
| | 1835 | 0.030 | 1770 | 0.268 | 9.0 |
| | 1812 (1845) | 0.050 | 1757 | 0.460 | 9.2 |

* R = alkyl.

** O.D. sym = optical density of the high frequency band.

*** O.D. asym = optical density of the low frequency band.

The large distance between the two bands ($70-80\text{ cm}^{-1}$) cannot be explained solely by a mechanic coupling of the two $\text{C}=\text{O}$ oscillators. Theoretically such a coupling should give a splitting no larger than $10-15\text{ cm}^{-1}$. The large splitting must be attributed to electronic effects [80].

In anhydrides of α, β -unsaturated acids, conjugation results in a $20-40\text{ cm}^{-1}$ decrease in frequency of the symmetric vibration. The second band (asymmetric vibration) maintains its position. Crotonic acid anhydride shows a doublet at 1780 and 1725 cm^{-1} . The same shift of the symmetric vibration toward lower

frequencies takes place in aromatic anhydrides. Benzoic anhydride absorbs at 1789 cm^{-1} and 1727 cm^{-1} [76].

In cyclic anhydrides cyclization acts in the opposite direction. Both bands shift toward higher frequencies. Strain-free six-membered ring anhydrides have almost the same frequency as aliphatic anhydrides. Glutaric anhydride absorbs at 1812 and 1764 cm^{-1} . However, the intensity ratio is different from that in acyclic anhydrides; whereas the intensity of the low frequency band remains practically the same as in acyclic compounds, the intensity of the high frequency band diminishes appreciably (the density ratio rises). In succinic anhydride (five-membered ring), the frequency increases (1866 and 1792 cm^{-1}) because of changes in hybridization determined by strain [53]. The intensity of the first band is of the same order of magnitude as in glutaric anhydride, whereas the intensity of the lower frequency band shows a large increase.

Band positions in five-membered ring anhydrides of 1,2-dicarboxylic acids (e. g. substituted succinic anhydrides) are not very sensitive to the mode of substitution. The situation is approximately the same when the succinic system is part of a cycloalkane ring (Table II-196). However, a rise in frequency is observed in the anhydride of *cis*-1,2-cyclopropanedicarboxylic acid cf. *cis*-1,2-cyclobutanedicarboxylic acid.

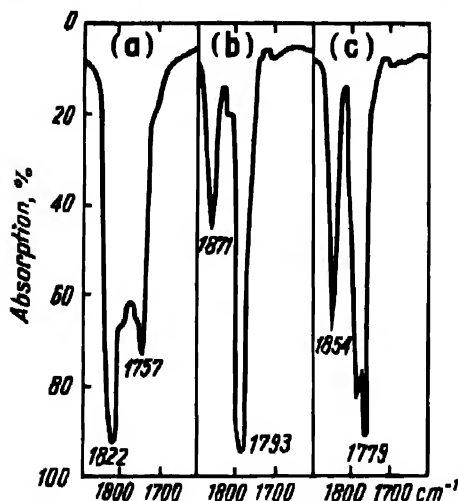


Fig. II-99

(a) Infrared spectra of acetic, (b) succinic, and (c) phthalic anhydride in the νCO region.

and 1775 cm^{-1} , and the anhydride of naphthalene 1,2-dicarboxylic acid absorbs at 1848 and 1783 cm^{-1} [76]. In the latter case the distance between the two bands is smaller [79].

Figure II-99 shows the νCO region in spectra of acetic, succinic and phthalic anhydrides [81]. Variations of relative band intensities and frequencies can be observed.

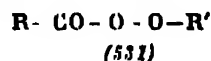
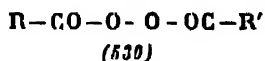
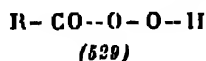
In anhydrides of unsaturated 1,2-dicarboxylic acids the effects of conjugation and cyclization seem to compensate each other and the frequencies of the doublet cannot be readily distinguished from those in acyclic anhydrides. Maleic anhydride absorbs at 1835 and 1770 cm^{-1} and dimethylmaleic anhydride, at 1812 and 1757 cm^{-1} [80]. The intensities of the two bands show the same behavior as in succinic anhydride. One or two methyl substituents at the double bond reduce the frequency of the weaker absorption by ca. 30 cm^{-1} (see Methyl and Dimethylmaleic anhydrides). Compensation of conjugation and cyclization effects is also observed in anhydrides of aromatic 1,2-dicarboxylic acids; for example, in phthalic anhydride the two bands occur at 1845

In anhydrides of α -halogenated acids, both bands are shifted toward higher frequencies; for example, trifluoroacetic anhydride $(F_3C-CO)_2O$ absorbs at 1884 and 1818 cm^{-1} [76].

A band occurring between 1160 and 1250 cm^{-1} seems to be characteristic for all cyclic and acyclic anhydrides [82].

D. PERACIDS, PERESTERS, AND PEROXIDES

Peracids (529) and peroxides (530) are derivatives of hydrogen peroxide and are formally obtained by replacement of one or both hydrogen atoms by acyl or aroyl group. In peresters (531) one of the hydrogen atoms is replaced by an acyl or aroyl group and the other one by a group R' alkyl or aryl.



Characteristic bonds in these compounds are the $O-O$ linkage and $C=O$ bonds in the acyl group. The absorption of the $O-O$ bond in hydrogen peroxide or in D_2O_2 is weak. The band occurs at 877 cm^{-1} in H_2O_2 and has approximately the same position in D_2O_2 [83]. In organic derivatives (529) (530) and (531), a weak absorption is expected in this region. However, it is difficult to identify since both its mass and force constant are very close to those of $C-O$ and $C-C$ bonds, and it cannot be distinguished from absorptions arising from these bonds. In a number of peracids the $O-O$ bond has been assigned a band between 830 and 890 cm^{-1} the same as in hydroperoxides [84, 85]. In turn, $C=O$ and $O-H$ absorptions are characteristic. Their frequencies are shifted due to the influence of the two adjacent oxygen atoms.

Acyl peroxides $RCO-O-O-OCR'$, where R and R' are the same alkyl group show two strong bands in the $C=O$ stretching mode region: 1810–1820 and 1785–1795 cm^{-1} . The distance between the two components of the doublet is ca. 25 cm^{-1} . Aroyl peroxides, with $R, R' =$ aryl, absorb at 1780–1805 and 1758–1784 cm^{-1} . In mixed acyl aroyl peroxides (530), with $R =$ alkyl and $R' =$ aryl, the frequencies of the two bands lie in the range 1796–1811 and 1771–1786 cm^{-1} . Frequencies of some acyl, aroyl, and mixed peroxides are shown in Table II-197.

The presence of a doublet in the νCO region was attributed to a coupling between the symmetric and antisymmetric vibration of the peroxidic system [86–88]. A splitting of the same type also occurs in anhydrides, but here the distance between the two absorptions is much larger (ca. 60 cm^{-1}) and is attributed to electronic effects [80]. Absorptions arising from peroxides occur at higher frequencies and the bands are sharper than in anhydrides.

In mixed acyl-aroyl peroxides the two $C=O$ absorptions have different frequencies (unperturbed). Acetylbenzoyl peroxide $CH_3CO-O-O-OCC_6H_5$ shows an absorption at 1811 cm^{-1} (Table II-197, Column 1) which may be assigned to the acetyl group (analogous to the 1808 cm^{-1} absorptions in $CH_3CO-O-O-OCCl_3$) and a second absorption at 1779 cm^{-1} (Column 2)

Table II-197 ν_{CO} frequencies in peroxides [88]

| RCO group | Solvent | $\nu_{\text{CO}}, \text{cm}^{-1}$ | | $\Delta \nu_{\text{CO}}$ | ν_{CO} mean |
|---------------------------------|-----------------------------------|-----------------------------------|------|--------------------------|------------------------|
| | | 1 | 2 | | |
| Aliphatic | | | | | |
| Acetyl | CCl_4 | 1820 | 1798 | 24 | 1808 |
| Octanoyl | " | 1812 | 1786 | 26 | 1799 |
| Lauroyl | " | 1811 | 1786 | 25 | 1798 |
| Miristoyl | " | 1811 | 1786 | 25 | 1798 |
| Stearoyl | " | 1811 | 1786 | 25 | 1798 |
| Aromatic | | | | | |
| Phthaloyl | Dioxane | 1800 | 1784 | 26 | 1794 |
| <i>p</i> -Nitrobenzoyl | $\text{C}_2\text{H}_4\text{Cl}_2$ | 1799 | 1779 | 20 | 1789 |
| <i>p</i> -Iodobenzoyl | " | 1792 | 1771 | 21 | 1781 |
| <i>p</i> -Bromobenzoyl | " | 1793 | 1771 | 22 | 1782 |
| <i>p</i> -Chlorobenzoyl | " | 1787 | 1765 | 22 | 1776 |
| <i>p</i> -Fluorobenzoyl | " | 1789 | 1778 | 21 | 1778 |
| Benzoyl | " | 1789 | 1767 | 22 | 1778 |
| <i>p</i> -Toluoyle | " | 1785 | 1763 | 22 | 1774 |
| <i>p</i> -Methoxy-benzoyl | " | 1780 | 1758 | 22 | 1769 |
| Mixed | | | | | |
| Acetyl-benzoyl | CCl_4 | 1811 | 1779 | 32 | 1795 |
| Stearoyl-benzoyl | " | 1811 | 1786 | 25 | 1798 |
| Benzoyl- <i>p</i> -nitrobenzoyl | " | 1797 | 1773 | 24 | 1785 |

assigned to the benzoyl group (analogous to the 1778 cm^{-1} absorption in $\text{C}_6\text{H}_5\text{CO}-\text{O}-\text{O}-\text{OCC}_6\text{H}_5$).

Table II-197 shows that in acyl peroxides the frequency does not vary with the chain length of the alkyl group. In *para*-substituted benzoyl peroxides a slight increase in mean frequency is observed for electron accepting substituents ($-I$ and $-E$ effect) and a decrease in frequency for electron-releasing substituents ($+E$ effect). This would favor the hypothesis that the vibration is sensitive to electronic effects. As expected, the influence is stronger in the asymmetric vibration. ($-I$, $-E$ effect in *p*-nitro cf. $-I$, $+E$ effect in *p*-methoxy).

Peresters $\text{R}-\text{CO}-\text{O}-\text{O}-\text{R}'$ show a single ν_{CO} absorption between 1758 and 1783 cm^{-1} (Table II-198), occurring sometimes between 1747 and 1820 cm^{-1} [88]. The characteristic frequency is readily distinguishable from the ν_{CO} frequency in normal esters ($1715-1765 \text{ cm}^{-1}$). This band is frequently used to determine the amount of perester present in a reaction mixture.

Table II-198 Characteristic ν_{CO} frequencies in peresters and peracids [88]

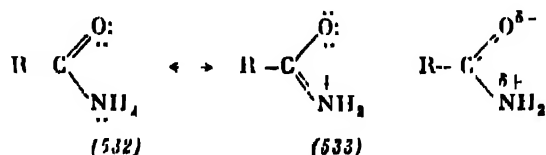
| Compound | Solvent | $\nu_{\text{CO}} \text{ cm}^{-1}$ |
|---------------------------------|----------------|-----------------------------------|
| <i>t</i> -Butyl peracetate | - | 1783 |
| <i>t</i> -Butyl-perbenzoate | - | 1758 |
| Di- <i>t</i> -butylperphthalate | CCl_4 | 1772 |
| Perbenzoic acid | CCl_4 | 1732 |

In perbenzoic acid the strong absorption at 1732 cm^{-1} corresponds to a $\text{C}=\text{O}$ bond perturbed by hydrogen bonding (for the free group a frequency of 180 cm^{-1} should be expected).

In the νOH region the band at 3259 cm^{-1} corresponds to the vibration of a bonded OH group (probably by intramolecular hydrogen bonding). Studies of relationships between the νCO frequency and the strength of $\text{O}-\text{O}$ bond, i.e. the case of decomposition of peroxides, have shown that the higher the νCO frequency, the weaker the $\text{O}-\text{O}$ and the $\text{O}-\text{H}$ bonds [88]. This is in agreement with the chemical properties of these compounds.

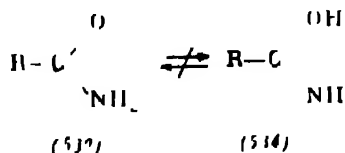
E. AMIDES

The functional group of amides has a strong internal $p-\pi$ conjugation represented by structures (532) and (533).

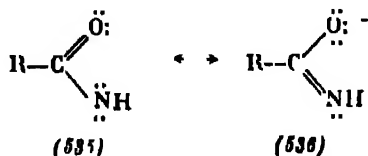


The greater mobility of the unshared electrons of nitrogen compared to oxygen and the less electronegative character of nitrogen favor structure (533). Because of this the $\text{C}-\text{O}$ bond order decreases, while the $\text{C}-\text{N}$ bond order increases. This results in a decrease in CO frequency and an increase in $\text{C}-\text{N}$ frequency.

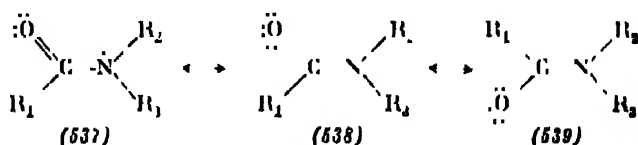
As regards the structure of the $-\text{CONH}_2$ group which is well-established both on theoretical and experimental grounds [89], infrared spectroscopy helped to confirm the amidic structure (532) and to rule out the tautomeric isoamidic structure (534).



In the mesomeric amide anion participation of structures (535) and (536) is approximately equal (the same as in the carboxylate anion).



Because of conjugation, the amide group is planar. Free rotation of the partially double C—N bond is hindered. This leads to *cis-trans* isomers (537)–(539) [89].



Amides have been extensively studied in the infrared, in connection with the structure of penicillin [90], the amidic linkage in peptides and proteins [91–93], and in urea derivatives [94]. Assignments of vibration modes have been discussed in several papers, and no general agreement seems to exist [95–102]. The difficulties are concerned with variations in frequency due to the various possibilities of conjugation mentioned above.

Characteristic frequencies in amides arise from C=O, C—N, and NH bonds (in primary and secondary amides, spectra of tertiary amides do not show the strong absorptions of the NH group). The absorptions occur in three regions of the spectrum: 3050–3550, 1470–1700, and 1300–1400 cm^{-1} . The first two are the most important.

Bands in the 3000 cm^{-1} region arise from N—H stretching vibrations in NH_2 and NHR groups. Primary amides (as well as primary amines) show two absorptions, corresponding to the asymmetric (540) and symmetric vibrations (541) of the NH_2 group. Secondary amides show a single band which in some instances is a doublet.



Spectra of secondary amides recorded in solution show two bands, due to *cis-trans* isomerism [(538)–(539), $\text{R}_2=\text{H}$].

Hydrogen bonding between C=O and N—H groups results in large band shifts, mainly in spectra of amides in the solid state [102a]. The degree and type of bonding can be followed in spectra of solutions at various concentrations. As in the case of hydroxyl compounds, the shape and position of absorption bands are of primary importance in the determination of molecular structure and configuration.

In the 1470–1700 cm^{-1} region, all amides show characteristic bands. Their number is determined by the structure of the molecule. The origin of these bands is not yet completely understood. The most important contribution is that of the C=O stretching vibration and of the N—H deformation vibration. The following terminology is commonly used: *amide I band*, assigned to the C=O stretching vibration, *amide II band*, assigned to the NH deformation vibration, and *amide III band*, assigned to the C—N stretching vibration, coupled with an NH vibration [22, 97, 98].

In recent years a strong trend has developed to treat the $-\text{CONH}_2$ group as a complex vibrational entity, involving stretching vibrations of

the C—O—N group and deformation vibrations of the NH_2 or NH group [100—102].

Checking of empirical assignments by isotopic labeling has confirmed the major contribution to the amide I band is due to the νCO vibration. The origin of amide II and amide III bands is controversial [101—102].

A band occurring at ca. 700 cm^{-1} , only in spectra of bonded secondary amides, is assigned to an out-of-plane deformation of the NH bond and is known as the *amide V band*.

Amide IV and *amide VI* bands have been assigned to skeletal vibrations. They occur at ca. 600 cm^{-1} in secondary amides and at ca. 1400 cm^{-1} in primary amides [97].

1. Primary amides

a. νNH vibration. In dilute solution primary amides absorb at ca. 3415 and 3530 cm^{-1} as a result of symmetric (547) and asymmetric (540) stretching vibrations of the NH_2 group [98, 103].

In saturated aliphatic amides with 2-12 carbon atoms, the sym νNH frequency lies in the range 3410 – 3413 cm^{-1} , and the asym νNH frequency occurs at 3526 – 3532 cm^{-1} (in chloroform) [98]. Band positions are not sensitive to chain length or branching. Isobutyramide absorbs at 3528 and 3412 cm^{-1} and isovalerylamide, at 3529 and 3412 cm^{-1} .

The intensity of νNH bands in aliphatic amides is higher than in the corresponding aliphatic amines.

In phenylacetamide the asym νNH frequency is 3519 cm^{-1} , while the sym νNH is 3407 cm^{-1} . In trichloroacetamide the frequencies are slightly lower: asym νNH is 3517 and sym νNH , 3403 cm^{-1} .

In concentrated solutions or in the solid state, hydrogen bonding results in shifts of νNH bands toward lower frequencies. On progressively increasing the concentration of simple amides in chloroform solution, the free νNH bands at 3530 and 3415 vanish completely, being replaced by two increasingly stronger, relatively narrow, bands at 3498 and 3182 cm^{-1} . They are accompanied by two weaker bands: 3345 and 3300 cm^{-1} [98, 104]. These absorptions are characteristic of intramolecular hydrogen bonding.

b. $\nu\text{C}=\text{O}$ vibration (*amide I band*). All primary amides have strong absorptions between 1650 and 1715 cm^{-1} . The position and intensity of this band depend on the nature of the solvent and on concentration. Its assignment to a fundamental vibration mode determined essentially by the $\text{C}=\text{O}$ linkage is justifiable. This band is known as the *amide I band*. It occurs in dilute solutions at 1675 – 1715 cm^{-1} and in concentrated solutions or in the solid state at 1650 – 1670 cm^{-1} . A decrease in frequency in the crystalline state is due to lattice forces.

In straight-chain n -alkylamides $\text{CH}_3-(\text{CH}_2)_n-\text{CONH}_2$, where $n=1\ldots 10$, dilute solutions in chloroform absorb at 1679 cm^{-1} . The dependence of band positions on solvent can be seen by comparing spectra of hexanoic acid amide in dioxane (1692 cm^{-1}), chloroform (1682 cm^{-1}), and methanol (1672 cm^{-1}).

The lowest frequency is observed in methanolic solutions, where alcohol-amide bonding is possible. In the solid state (KBr) these compounds absorb at $1655\text{--}1667\text{ cm}^{-1}$ [105] (Fig. II-100).

Acetamide shows special behavior. In the solid state it has a single band at 1694 cm^{-1} (in nujol) or at 1679 cm^{-1} in KBr [22, 95, 105, 106].

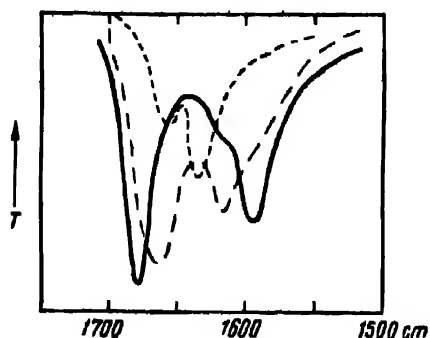


Fig. II-100 Infrared spectrum of hexanoic acid amide. Dotted line—solid state; - - - concentrated solution in CHCl_3 ; solid line—dilute solution in CHCl_3 .

Spectra recorded in solution show a doublet with the two components at 1714 and 1695 cm^{-1} in carbon tetrachloride, at 1709 and 1681 cm^{-1} in acetonitrile, and at $1700\text{--}1678\text{ cm}^{-1}$ in chloroform [104]. In higher aliphatic amides in concentrated solution the band becomes broader and the frequency decreases. In hexanoic acid amide the 1655 cm^{-1} band corresponding to the solid state occurs at 1668 cm^{-1} in concentrated solution and at 1680 cm^{-1} in dilute solution.

Band shifts toward higher frequencies on passing from the solid state to dilute solution have been attributed to a larger contribution of the amidic

structure (532), rather than of the polar structure (533). The latter is favored in the solid state, due to hydrogen bridges $\text{C}=\text{O}\cdots\text{H}-\text{N}$, resulting in a lower $\text{C}=\text{O}$ bond order.

The sensitivity of this absorption to experimental conditions makes comparisons possible only in spectra recorded under identical conditions.

Characteristic frequencies of some amides in the solid state (KBr) are shown in Table II-199.

The integrated absorption of aromatic amides ($B \cdot 10^{-2} = 218$) is higher than in aliphatic compounds ($B \cdot 10^{-2} = 113$). This is because of conjugation of the $-\text{CONH}_2$ group with the aromatic ring enhancing the polar character of the $\text{C}=\text{O}$ bond.

Table II-199 Characteristic frequencies (cm^{-1}) in amides [22]

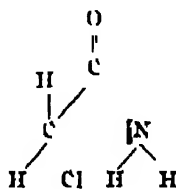
| Compound | Amide I band (ν_{CO}) | Amide II band (δNH_2) | Amide III band |
|--------------------|------------------------------------|---------------------------------------|----------------|
| Acetamide | 1679 | 1625 | 1395 800 |
| Propionamide | 1670 | 1637 | 1425 823 |
| n-Butyramide | 1667 | 1641 | 1439 813 |
| Benzamide | 1663 | 1631 | 1408 793 |
| p-Nitrobenzamide | 1673 | 1620 | |
| p-Methoxybenzamide | 1678 | 1624 | |
| p-Chlorobenzamide | 1667 | 1628 | |
| p-Aminobenzamide | 1623 | 1605 | |

In the solid state, frequency differences between amide I bands in the aliphatic and aromatic series are not readily noticeable. For this reason, relationships between νCO frequency or absorption intensity and the electronic effect of substituents have been studied in solution. Benzamide has been the most extensively investigated. Spectra of benzamide- ^{18}O [101], benzamide- ^{15}N , and benzamide- D_2 ($\text{C}_6\text{H}_5\text{COND}_2$) [100] have been compared in solution and in the solid state [102]. In carbon tetrachloride solution the amide I band of normal free benzamide occurs at 1690 cm^{-1} . In the O^{18} -labeled compound the frequency of this band decreases by 24 cm^{-1} (1666 cm^{-1}), a value comparable with that due to an isotope effect in benzophenone- ^{18}O . This is a further argument for assignment of the amide I band to a vibration of a predominantly $\nu\text{C}-\text{O}$ character [101, 107]. Another strong argument is the fact that in N^{15} -labeled compounds the amide I band remains unchanged, whereas the amide II band is shifted because of an isotope effect. In the liquid state hydrogen bonding and dipole interactions result in a large decrease in νCO frequency (to 1620 cm^{-1}) [112, 118].

In carbon tetrachloride the νCO band intensity of $\text{C}_6\text{H}_5\text{C}^{18}\text{ONH}_2$ is 20% higher than in $\text{C}_6\text{H}_5\text{C}^{16}\text{ONH}_2$. A similar rise in intensity (15%) is observed on isotopic substitution of the $\text{C}=\text{O}$ group in benzophenone- ^{18}O [109]. In chloroform no intensity changes between the normal and labeled compound are observed. It is assumed that in this case interactions between chloroform and benzamide- ^{16}O and ^{18}O are different [101]. Table II-200 shows the intensity of amide I bands in $\text{C}_6\text{H}_5\text{C}^{16}\text{ONH}_2$ and $\text{C}_6\text{H}_5\text{C}^{18}\text{ONH}_2$ [22].

Table II-200 Amide I band intensities in labelled benzamides

| Compound | Frequency cm^{-1} | Thickness of layer, mm | Concen- trations g/l | Solvent | Optical density | Molar extinction coefficient $1\text{ mole}^{-1}\text{ cm}^{-1}$ |
|---|-------------------------------|------------------------------|----------------------------|-----------------|--------------------|---|
| $\text{C}_6\text{H}_5\text{C}^{16}\text{ONH}_2$ | 1690 | 20 | 0.052 | CCl_4 | 0.440 | 720 |
| $\text{C}_6\text{H}_5\text{C}^{18}\text{ONH}_2$ | 1666 | 20 | 0.055 | CCl_4 | 0.479 | 580 |
| $\text{C}_6\text{H}_5\text{C}^{16}\text{ONH}_2$ | 1675 | 1 | 1.40 | CHCl_3 | 0.664 | 578 |
| $\text{C}_6\text{H}_5\text{C}^{18}\text{ONH}_2$ | 1655 | 1 | 1.39 | CHCl_3 | 0.61 | 690 |



(548)

The influence of a halogen atom in the α -position on the νCO frequency is difficult to study in amides because of reduced solubility and of hydrogen bonding in the solid state. However, the halogen atoms seem to have a different

effect from that in esters or ketones. Monochloroacetamide absorbs at 1653 cm^{-1} (in KBr) and monoiodoacetamide, at 1671 cm^{-1} . Trichloroacetamide $\text{Cl}_3\text{C}-\text{CONH}_2$ absorbs at 1703 cm^{-1} in the solid state (in KBr) and at 1732 cm^{-1} in 0.01 in solution in chloroform [8, 22, 105]. The frequency increases with the number of halogen atoms.

It is assumed that in solution and in the solid state the conformational isomer (542) is present. It is favored due to intramolecular $\text{Cl} \cdots \text{N}-\text{H}$ bond and electrostatic repulsion between chlorine and oxygen [7, 110].

c. **Amide II band.** In the $1580-1650\text{ cm}^{-1}$ region primary amides show a second, weaker band of variable position, depending on the solvent and the structure and physical state of the amide.

In spectra of straight-chain alkylamides $\text{CH}_3-(\text{CH}_2)_n\text{CONH}_2$, where $n=1, 2, \dots, 10$, the absorption occurs at $1588-1590\text{ cm}^{-1}$ (in dilute chloroform solution) [105].

The intensity of the amide II band is twice or three times less than that of amide I band ($\epsilon_{\text{max}}^{(a)}=180 \dots 210$) [90]. The intensity of this band decreases in more concentrated solutions, whereas the frequency increases. Solid alkylamides $\text{R}-\text{CONH}_2$ with 3-12 carbon atoms absorb at $1620-1650\text{ cm}^{-1}$ [105, 111].

The amide II band occurs only in primary and secondary amides with two hydrogen atoms or one hydrogen atom, respectively, on nitrogen [96]. It does not occur in tertiary amides. For this reason, by analogy with the $\text{N}-\text{H}$ deformation vibration in amines, the origin of this band was associated with a deformation of the $\text{N}-\text{H}$ bond [96, 105, 111].

Some authors have suggested more complicated assignments for amide I and amide II bands, involving both $\text{C}=\text{O}$ stretching vibrations and NH deformation vibrations [93, 111].

d. **Other vibrations.** Spectra of primary amide consistently show a band at $1399-1418\text{ cm}^{-1}$ [95, 97, 100], not observed in spectra of secondary and tertiary amides. This absorption is assigned to a $\text{C}-\text{N}$ vibration; however, its analytical value is not significant. This band occurs at 1395 cm^{-1} in acetamide (in KBr) and at 1425 cm^{-1} in propionamide (in KBr) [22] or at 1375 cm^{-1} (in CCl_4) [101, 102]. Its intensity changes in ^{18}O labeled compounds [101]. Some workers assign this band to a vibration involving both $\text{C}-\text{N}$ stretching mode and NH deformation mode [95, 97].

2. Secondary amides

a. **NH stretching vibration.** In dilute solution secondary amides show a single absorption in the NH stretching vibration region, assigned to free $\text{N}-\text{H}$ bonds [112]. *N*-alkylamides and cyclic imides in chloroform solution absorb between 3400 and 3170 cm^{-1} . *N*-Arylamides absorb at 3500 cm^{-1} . The intensity of the free νNH band decreases in concentrated solutions. In the solid state the band vanishes, but two new bands appear instead: $3280-3330$ and $3060-3100\text{ cm}^{-1}$, assigned to hydrogen-bonded molecules [31, 98, 103].

N-Methylacetamide absorbs at 3465 and 3340 cm^{-1} (0.07 M solution in chloroform) and at 3465s, 3330m, and 3090w cm^{-1} (0.3 M solution). At higher concentrations, the intensity of the 3465 cm^{-1} band decreases while that of the 3330 cm^{-1} band increases substantially, and the 3090 cm^{-1} band becomes better defined [98] (Fig. II-101).

The absorptions of bonded forms have been extensively studied in peptides and proteins [113, 114]. The origin of the bands is still under discussion.

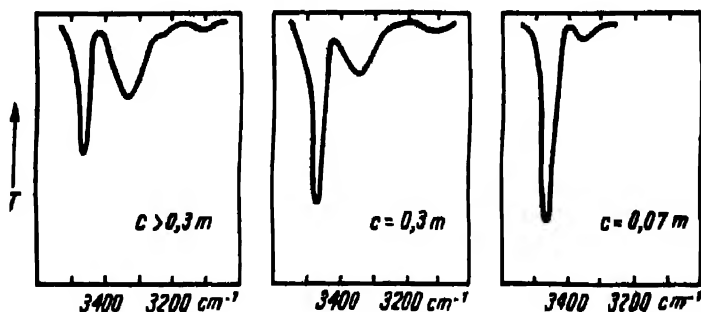
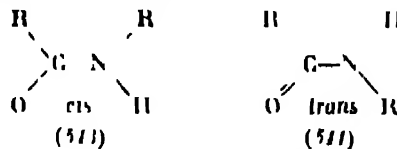


Fig. II-101 Infrared spectrum of *N*-methylacetamide in the N-H region at various concentrations in chloroform.

Their intensity varies from α to β forms of polypeptide chains. The bands show dichroism. The two absorptions are assigned to N-H ... O=C and not to N-H ... N hydrogen bonds [96].

νNH absorptions have been suggested for the identification of *cis* and *trans* isomers in substituted amides [103, 115–117]. *cis* Forms (543) have lower frequencies (3420–3440 cm^{-1}), whereas *trans* forms (544) have slightly higher frequencies (3440–3460 cm^{-1}) [103].

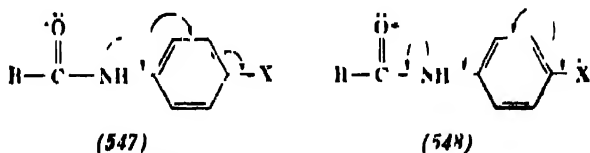
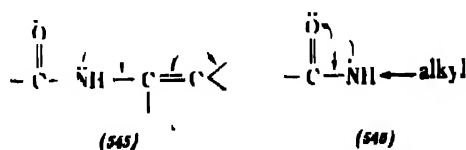


Using these criteria it has been established, that *N*-phenylbenzamide $\text{C}_6\text{H}_5\text{CONH}-\text{C}_6\text{H}_5$ with a single absorption at 3440–3460 cm^{-1} is in the *trans* form exclusively. The same is true for *N*-methylacetamide $\text{CH}_3-\text{CONH}-\text{CH}_3$. In sterically hindered amides (e. g., *N*-*t*-butylphenylacetamide) the predominant form is *cis* (70%) [117].

b. νCO stretching vibration (amide I band). The νCO frequency in secondary amides $\text{R}-\text{CONH}-\text{R}'$ depends on the nature of groups R and R', the physical state, the concentration, and the nature of the solvent. The lowest frequency is observed in the solid state because of hydrogen bonding. Amides where R and R' are alkyl groups absorb in the solid state at 1640 cm^{-1} [90, 95, 96, 105, 106, 118]. In dioxane solutions the band occurs at 1675–1680 cm^{-1} [96]. In chloroform, *N*-methylacetamide absorbs at 1671 cm^{-1} with

an $\epsilon_{\text{max}}^{(a)} = 55'$ [105]. *N*-Arylamides have higher frequencies under the same conditions. The increase in frequency is due to conjugation between the benzene ring and the nitrogen atom. This weakens the internal conjugation of the CO—NH group, increasing the C=O bond order (545). In *N*-alkyl derivatives the internal conjugation (546) is favored. Substituents in the benzene ring of *N*-phenylacetamides affect the $\nu\text{C}=\text{O}$ frequency by favoring either structure (547) or (548).

Electron releasing substituents with a strong $+E$ effect reduce the frequency, whereas substituents with $-I$, $-E$ effects increase the νCO frequency. Table II-201 shows frequencies of amide I and amide II bands in *para* substituted acetanilides [22].



strong $-I$ effect $\left\{ \begin{array}{l} \nu\text{CO} \\ \text{rises} \end{array} \right.$ weak $-I$ $\left\{ \begin{array}{l} \nu\text{CO} \\ \text{falls} \end{array} \right.$ strong $-I$ $\left\{ \begin{array}{l} \nu\text{CO} \text{ does not change} \\ \text{or rises slightly} \end{array} \right.$
 strong $+I$ effect $\left\{ \begin{array}{l} \nu\text{CO} \\ \text{rises} \end{array} \right.$ strong $+E$ $\left\{ \begin{array}{l} \nu\text{CO} \\ \text{falls} \end{array} \right.$ weak $+E$ $\left\{ \begin{array}{l} \nu\text{CO} \text{ does not change} \\ \text{or rises slightly} \end{array} \right.$

Table II-201 Frequencies of amide I and amide II bands (cm^{-1}) in substituted acetanilides (in KBr)

| Compound | Formula | Frequency | |
|-----------------------------|---|-----------|----------|
| | | Amide I | Amide II |
| Acetanilide | $\text{CH}_3-\text{CONH}-\text{C}_6\text{H}_5$ | 1670 | 1561 |
| <i>p</i> -Methylacetanilide | $\text{CH}_3-\text{CONH}-\text{C}_6\text{H}_4\text{CH}_3$ | 1671 | 1539 |
| <i>p</i> -Chloroacetanilide | $\text{CH}_3-\text{CONH}-\text{C}_6\text{H}_4\text{Cl}$ | 1673 | 1545 |
| <i>p</i> -Nitroacetanilide | $\text{CH}_3-\text{CONH}-\text{C}_6\text{H}_4\text{NO}_2$ | 1688 | 1585 |

It should be pointed out that the decrease in frequency of the $\nu\text{C}=\text{O}$ (amide I) band is accompanied by an increase in frequency of the amide II band. In secondary amides of aromatic acids, the $\nu\text{C}=\text{O}$ vibration is altered both by the effect of the aromatic ring and the group R' attached to nitrogen. *N*-Phenylbenzamide has a higher frequency than *N*-alkylbenzamide, due to the conjugation mentioned in the case of *N*-phenylamides of aliphatic acids. $\text{C}_6\text{H}_5-\text{CONH}-\text{C}_6\text{H}_5$ absorbs at 1663 cm^{-1} , and $\text{C}_6\text{H}_5-\text{CONH}-\text{CH}_2-\text{C}_6\text{H}_5$ at 1651 cm^{-1} (KBr) [22].

In *p*, *p'*-disubstituted *N*-phenylbenzamides $\text{Y}-\text{C}_6\text{H}_4-\text{CO}-\text{NH}-\text{C}_6\text{H}_4-\text{X}$, the electronic effect of substituents X and Y alters the amidic conjugation

favoring structures (532) or (533). Electron releasing groups reduce the $C=O$ bond order favoring structure (533) and the frequency decreases. In the *p*, *p'*-dimethylamino derivative ($X=Y=N(CH_3)_2$), the frequency decreases to 1635 cm^{-1} . Electron attracting groups favor structure (532) and the frequency increases. In the *p*, *p'*-dinitro derivative ($X=Y=NO_2$), the frequency increases to 1685 cm^{-1} . If *X* and *Y* have opposite effects, they compensate each other and the $\nu C=O$ frequency remains practically unchanged cf. the unsubstituted compound [118].

c. Amide II band. In spectra of secondary amides the second absorption known as the amide II band occurs between 1475 and 1580 cm^{-1} . Its intensity is lower than that of the amide I bands. In *N*-alkylamides of aliphatic acids, it occurs at $1530 - 1540\text{ cm}^{-1}$ (dioxane solution). Because of its position and intensity, this band can be distinguished from absorptions of primary amides ($1615 - 1620\text{ cm}^{-1}$). In the solid state the frequency decreases to 1560 cm^{-1} , and the band position is much more variable than in spectra recorded in solution [96, 119]. The frequency of the amide II band in solution is lower than in the solid state, opposite to the behavior of the amide I (νCO) band. *

The origin of this band has prompted many discussions [22, 105]. It has been assigned to a $C-N$ or $C=N$ stretching vibration or to a $N-H$ deformation vibration (by analogy with the δNH_2 vibration in primary amines [96]). In this instance deuteration experiments were not conclusive. On progressively replacing the amide hydrogen atoms by deuterium, the intensity of the amide II band decreases and two new bands occur: 1470 cm^{-1} (strong) and 1130 cm^{-1} . They were assigned to $N-D$ deformation vibrations [90, 120].

The assignment of this band to a $C-N$ stretching vibration with a marked double bond ($C=N$) character seems to be favored by the increase in frequency and band intensity. On the other hand, the amide II band does not occur in tertiary amides.

N-Methyl acetamide absorbs at 1490 cm^{-1} , and in dilute chloroform solutions at 1533 cm^{-1} ($\epsilon_{max}^{(a)} = 200$). Because of its sharpness, this band was assigned to the monomeric form [121] in contradiction with some authors who assign it to the dimer [120].

In the case of secondary amides (extensively studied in connection with peptide structures) a more plausible interpretation seems to be that in which the amide II band is considered to arise from a complex vibration that involves all the atoms of the group [100, 101].

The peptide bond involves an appreciable internal conjugation that can be perturbed by rotation about the $C-N$ bond and by steric factors inhibiting the coplanarity of the system.

d. Amide III band. Secondary amides have a weak absorption between 1290 and 1300 cm^{-1} assigned to vibrations involving $O-C-N$ and $N-H$ bonds [92, 93, 109, 122, 123]. The position of this absorption is altered on deuteration and change in physical state, which demonstrates the contribution of nitrogen and hydrogen atoms to this vibration.

e. Amide IV and amide VI bands. Absorptions of secondary amides in the low frequency region (at 600 and 620 cm^{-1}) [109, 118, 123, 124] are

assigned to skeletal vibrations; however, they are not sufficiently characteristic to be used for analytical purposes.

f. **Amide V band.** This absorption at ca. 720 cm^{-1} occurs only in bonded secondary amides. It was assigned to a N-H deformation [123]. *N*-Methylacetamide (dilute chloroform solution) shows a band at 648 cm^{-1} . On deuteration the band vanishes, being replaced by another one at 530 cm^{-1} [123, 125]. This band occurs both in polyamides and proteins.

3. Tertiary Amides

Tertiary amides show a single absorption in the $1550\text{--}1650\text{ cm}^{-1}$ region arising from the stretching vibration of the $\text{C}=\text{O}$ bond. In compounds $\text{R}-\text{CONR}_1\text{R}_2$ ($\text{R}=\text{R}_1=\text{R}_2=\text{alkyl}$), the band occurs at 1650 cm^{-1} (in dioxane) [96]. The frequency varies with the nature of the solvent. It decreases in more polar solvents capable of hydrogen bonding. νCO frequencies of *N,N*-diethylacetamide in dioxane, chloroform, and methanol are shown below.

| $\text{CH}_3-\text{CON} \begin{array}{l} \nearrow \text{C}_2\text{H}_5 \\ \searrow \text{C}_2\text{H}_5 \end{array}$ | Dioxane | Chloroform | Methanol |
|--|-----------------------|-----------------------|------------------------------------|
| | 1647 cm^{-1} | 1629 cm^{-1} | 1615 cm^{-1} (broad band) |

In *N,N*-disubstituted amides, which lack the amidic hydrogen atom and hence the possibility to form hydrogen bonds, the νCO frequency does not vary with physical state [96]. The only noticeable phenomenon is broadening of the band when alcohols are used as solvents.

The position of the νCO band is affected by the R group of the acid and by the groups R_1 and R_2 attached to nitrogen, as in the case of the other amides [22, 126].

| | | | |
|---|-----------------------|--|-----------------------|
| $\text{Alkyl}-\text{CO}-\text{N} \begin{array}{l} \nearrow \text{Alkyl} \\ \searrow \text{Alkyl} \end{array}$ | 1650 cm^{-1} | $\text{Aryl}-\text{CO}-\text{N} \begin{array}{l} \nearrow \text{Alkyl} \\ \searrow \text{Alkyl} \end{array}$ | 1640 cm^{-1} |
| $\text{Alkyl}-\text{CO}-\text{N} \begin{array}{l} \nearrow \text{Alkyl} \\ \searrow \text{Aryl} \end{array}$ | 1667 cm^{-1} | $\text{Aryl}-\text{CO}-\text{N} \begin{array}{l} \nearrow \text{Alkyl} \\ \searrow \text{Aryl} \end{array}$ | 1640 cm^{-1} |
| $\text{Alkyl}-\text{CO}-\text{N} \begin{array}{l} \nearrow \text{Aryl} \\ \searrow \text{Aryl} \end{array}$ | 1677 cm^{-1} | $\text{Aryl}-\text{CO}-\text{N} \begin{array}{l} \nearrow \text{Aryl} \\ \searrow \text{Aryl} \end{array}$ | 1650 cm^{-1} |

The effect of substituents on the $\text{C}=\text{O}$ bond order can be seen by comparing the frequencies shown. Variations correspond to the *I* and *E* effects of these groups.

In aryl $-\text{CO}-$ compounds, conjugation of the $\text{C}=\text{O}$ group with the benzene ring results in a decrease in νCO frequency (Table II-202). In *N*-aryl compounds, the phenyl group is conjugated with the unshared electrons of nitrogen, favoring the carbonyl structure. The νCO frequency increases. The

Table II-202 Frequencies of I, II, and III bands in tertiary amides (cm^{-1}) [22]

| Compound | Band | | |
|---|-------------|----------|-----------|
| | Amide I | Amide II | Amide III |
| $\text{C}_6\text{H}_5\text{CO}-\text{N} \begin{cases} \text{CH}_3 \\ \text{CH}_3 \end{cases}$ <i>N, N</i> -Dimethylbenzamide | 1639 (312)* | 1399 | 1266 |
| $\text{CH}_3-\text{CO}-\text{N} \begin{cases} \text{CH}_3 \\ \text{C}_6\text{H}_5 \end{cases}$ <i>N</i> -Methylacetanilide | 1667 (334)* | 1429 | 1299 |
| $\text{C}_6\text{H}_5\text{CO}-\text{N} \begin{cases} \text{CH}_3 \\ \text{C}_6\text{H}_5 \end{cases}$ <i>N</i> -Methylbenzanilide | 1649 (430)* | 1422 | 1304 |

* $\epsilon_{\text{mix}}^{(a)}$

† *I* effect of the alkyl group lowers the frequency. In *N*-methylbenzanilide the two effects compensate each other to a certain extent and the frequency has an intermediate value.

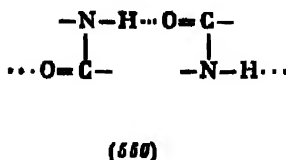
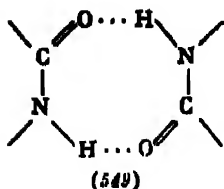
4. Cyclic Amides (Lactams)

Lactams are cyclic amides of amino acids and show some characteristic absorptions associated with their cyclic nature.

a. $\nu\text{N}-\text{H}$ vibrations. In dilute solution spectra of lactams show certain analogies with those of acyclic secondary amides. They have a band at 3420 cm^{-1} and another band at 3220 cm^{-1} of variable position depending on concentration [127].

In the solid state this absorption occurs at 3157 cm^{-1} and is accompanied by a weaker band (cf. acyclic amides) at 3080 cm^{-1} assigned to a bonded form [128].

Because the absorption at 3175 cm^{-1} occurs only in cyclic secondary amides it was assigned to the bonded *cis* form (549) [129–131].



The band occurring at 3280 cm^{-1} in aliphatic chains was assigned to the *trans* bonded form (550).

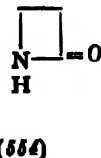
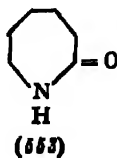
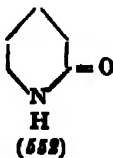
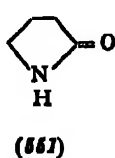
In large rings (e. g. nine-membered) which can exist also in the *trans* form, the band reappears [129, 130].

b. νCO vibrations. The νCO frequency in lactams depends on ring size. Lactams have been investigated extensively with regard to structures of natural products (mainly penicillin) [95, 128, 132, 133].

Frequency shifts in various lactam rings, cf. normal values in acyclic compounds are, listed below.

| Number of atoms | $\Delta\nu\text{CO}, \text{cm}^{-1}$ |
|-----------------|--------------------------------------|
| 5 | +31 |
| 6 | -13 |
| 7 | -15 |

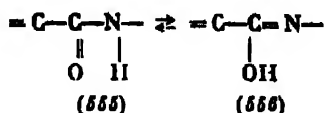
1. *Lactams with 5, 6 and 7-membered rings.* The νCO frequency is higher in the strained five-membered ring (γ -lactams) than in larger rings [53, 129, 131]. It varies with solvent and physical state (see Lactones).



In the vapor phase γ -butyrolactam (551) absorbs at 1754 cm^{-1} [93]. In the liquid state or in solution the frequency varies between 1680 and 1706 cm^{-1} : 1680 in the liquid phase [134], 1690 in chloroform [130, 134], and 1706 in carbon tetrachloride [131]. In the six-membered ring of δ -lactams (552) and the seven-membered ring of ϵ -lactams (553), the band occurs at ca. 1665 ± 5 in chloroform and $1680 \pm 10\text{ cm}^{-1}$ in carbon tetrachloride. In the solid state (KBr), the frequency decreases to 1645 cm^{-1} [134].

2. *Four-membered ring lactams.* β -Lactams (554) have been extensively studied in connection with the structure of penicillin [128, 135]. In penicillins the νCO absorption occurs at 1765 cm^{-1} . In simple β -lactams it occurs at $1770\text{--}1786\text{ cm}^{-1}$ [136-138]. In condensed rings or in the neighbourhood of polar groups (in the α -position), the frequency increases [128, 132, 135], reaching 1800 cm^{-1} in penicillin-sulfones and as high as 1900 cm^{-1} in other systems [133, 139].

In unsaturated γ - and δ -lactams, the pattern is more complicated because of the possible tautomerism (555) \rightleftharpoons (556)



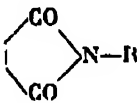
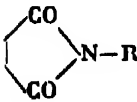
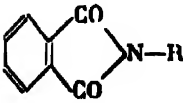
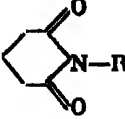
Lactam forms absorb at ca. 1680 cm^{-1} . In lactam forms the OH group absorbs at 3413 cm^{-1} [135].

5. Cyclic Imides

Cyclic imides show frequency variations dependent on ring size, the same as anhydrides of dicarboxylic acids. Imides show two $\nu\text{C=O}$ bands due to vibrational coupling of the two C=O bands. The symmetrical vibration has higher frequencies [110]. Five-membered ring imides have higher frequencies than those with strain-free six- and seven-membered rings.

Frequencies of some characteristic compounds are shown in Table II-203.

Table II-203 $\nu\text{C=O}$ frequencies (cm^{-1}) in cyclic imides

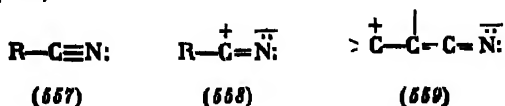
| Compound | R | State | $\nu\text{C=O}$ sym | $\nu\text{C=O}$ asym | References |
|---|--|------------------------------|---------------------------|---------------------------|---------------------|
|  | Alkyl H, C_6H_5 , Br | solid in CHCl_3 | 1779–1789 1776 1776 | 1695–1712 1718 1718 | [141] [142] |
|  | Alkyl, H | in KBr | 1751–1792 | 1686–1736 | [143] |
|  | H CH_3 | in CHCl_3 in KBr | 1772–1780 1744–1775 | 1712–1736 1685–1720 | [140, 144] [145] |
|  | CH_3 | solid | 1723 | 1672 | [141] |

In a number of substituted phthalimides linear relationships between frequency and Hammett- σ constants have been observed [145].

E. NITRILES

Nitriles are functional derivatives of carboxylic acids containing the group $\text{C}\equiv\text{N}$.

The distribution of electrons in the CN group can be represented by structures (557) and (558).



In compounds where the CN group is attached to an electron-releasing atom or group, structure (559) is also involved due to possible conjugative effects. The larger contribution of one of the three forms is determined primarily by the nature of the group R.

The electronegative nitrogen atom makes the carbon atom more positive, and the polar CN group has a $-I$ (electron-attracting) effect on the adjacent bond.

Measurements of interatomic distances as well as Raman and infrared spectra have shown that the predominant form is (557) with a triple bond between carbon and nitrogen [146].

The infrared absorption of nitriles occurs in the triple bond region, between 2000 and 2300 cm^{-1} . Increase or decrease in frequency of the $\text{C}\equiv\text{N}$ stretching vibration depends on the electronic effect of atoms or groups attached to CN [147].

For the first member of the series of nitriles of monocarboxylic acids, vibrational analyses have been carried out in both the infrared and Raman [148].

a. **Hydrogen cyanide.** The nitrile of formic acid or hydrogen cyanide $\text{H}-\text{C}\equiv\text{N}$ has the CN group attached to a hydrogen atom. In forming the triple bond between carbon and nitrogen, the carbon atom participates with an sp orbital, determining the linear configuration of the molecule the same as in the acetylene molecule. Because of the electron-attracting effect of nitrogen, the carbon atom becomes more positive, resulting in an increase in frequency and in intensity of the absorption.

Theoretically the linear triatomic molecule of hydrogen cyanide has three fundamental vibration modes shown in Fig. I-44 [149].

In vibration ν_1 , the outside atoms oscillate in opposite directions, whereas in vibration ν_2 , they oscillate in the same direction. To maintain the center of gravity of the molecule, the direction of motion of the carbon atom in ν_1 is opposite to that in ν_2 . This implies that vibration ν_1 (2089 cm^{-1}) has to be almost exclusively a $\text{C}\equiv\text{N}$ stretching vibration, and vibration ν_2 (3312 cm^{-1}) a C-H stretching vibration where the $\text{C}\equiv\text{N}$ group is nearly immobile. This vibration mode is a typical example of *group frequency* (see page 98). The doubly degenerate deformation vibration ν_3 occurs at 712 cm^{-1} .

Table II-204 shows vibration frequencies in some simple nitriles.

It can be seen that in halogenated compounds (see Fig. I-44) changes in mass ratios, cf. HCN , make the ν_1 vibration almost exclusively a C-Cl stretching vibration and ν_2 , a $\text{C}\equiv\text{N}$ stretching vibration. The decrease in ν_2 fre-

quency in halogenated compounds is due almost exclusively to a mass effect.

b. **Saturated nitriles.** The $\text{C}\equiv\text{N}$ stretching vibration in nitriles of saturated mono- and polycarboxylic acids lies in the range $2240\text{--}2260\text{ cm}^{-1}$ [147].

In the infrared, acetonitrile has a strong band at 2283 cm^{-1} , corresponding to the 2249 cm^{-1} band in the Raman spectrum [147]. Dilute solutions in chloroform show two bands: 2292 and 2255 cm^{-1} [38], whereas solutions in carbon tetrachloride show a single band at 2251 cm^{-1} [150]. The frequency decreases along the series of saturated aliphatic nitriles, varying from 2247 to 2241 cm^{-1} for $\text{R}=\text{C}_3\text{--}\text{C}_5$ (Table II-205). This small decrease in frequency is related to the more powerful electron-donating +I effect of the methyl group in acetonitrile [38, 150, 151].

Table II-204 Fundamental frequencies in X-CN molecules

| Molecule | Frequency, cm^{-1} | | |
|--------------------|-----------------------------|-----|------|
| | | | |
| HCN | 2089 | 712 | 3312 |
| DCN | 1908 | 568 | 2620 |
| C ₂ HCN | 729 | 397 | 2201 |
| BrCN | 580 | 368 | 2187 |
| ICN | 470 | 321 | 2158 |

Table II-205 $\nu\text{C}\equiv\text{N}$ frequencies (cm^{-1}) in saturated nitriles

| Compound | Liquid [151] | Solution in CHCl_3 [38] | Solution in CCl_4 [152] |
|--|--------------|----------------------------------|----------------------------------|
| CH_3CN | 2283 | 2292 2255 | 2251 |
| $\text{C}_2\text{H}_5\text{CN}$ | 2257 | | |
| $\text{C}_3\text{H}_7\text{CN}$ | 2247 | 2253 | 2250 |
| $\text{C}_4\text{H}_9\text{CN}$ | 2245 | | |
| $\text{C}_5\text{H}_{11}\text{CN}$ | 2241 | — | — |
| $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$ | 2273 | — | |
| $\text{CH}_2(\text{CN})_2$ | — | 2292 | 2273 |
| $\text{NC-CH}_2\text{-CH}_2\text{-CN}$ | | 2275 | 2256 |
| $\text{ROOC-CH}_2\text{-CN}$ | | 2270 | ($\nu\text{CO } 1751$) |

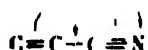
In aliphatic nitriles the intensity of the $\nu\text{C}\equiv\text{N}$ band is low [150].

In the linear molecule of dicyanide, resonance between the two CN groups results in a splitting of the $\text{C}\equiv\text{N}$ band. In general, the greater the distance between the components, the stronger is the coupling [152]. Absorptions occurring in $(\text{CN})_2$ at 2149 and 2322 cm^{-1} correspond to the 2089 cm^{-1} frequency in HCN [149].

In dinitriles with the two CN groups attached to the same carbon atom, the stronger -I effect of these groups results in shifts toward higher frequencies. The νCN frequency of malonodinitrile is 18 cm^{-1} higher than in saturated aliphatic nitriles [38]. The carbethoxy group in cyanoacetic ester shows the same effect, i. e. the $\nu\text{C}\equiv\text{N}$ frequency increases by 12 cm^{-1} . In this case the -I effect of the CN group also causes an increase in the νCO frequency in COOR (to 1751 cm^{-1} cf. 1741 cm^{-1} in ethyl acetate) [38]. The interaction of the two

CN groups diminishes in higher members of the series. The frequency in succinodinitrile (2256 cm^{-1}) is very little changed.

c. **Unsaturated nitriles.** In α, β -unsaturated nitriles, conjugation of the electrons of the double bond with the $\text{C}\equiv\text{N}$ group results in a decrease in frequency of both groups because of a decrease in $\text{C}=\text{C}$ and $\text{C}\equiv\text{N}$ bond orders.



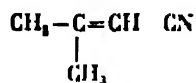
(560)

The $-I$ effect of the CN group and the $\text{C}=\text{C}$ double bond acting in opposite directions are dominated by the conjugative effect (560).

The νCN frequency decreases by ca. 35 cm^{-1} [147]. In acrylonitrile the absorption occurs at 2232 cm^{-1} [38, 148, 153]. In the homologous series of unsaturated nitriles, this frequency is $2225 \pm 8\text{ cm}^{-1}$ [147]. Crotonitrile and methacrylonitrile absorb at the same frequency, which shows that the inductive effect of the CH_3 group is transmitted through the double bond [38].

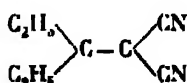
In *cis-trans* isomers differences in frequency do not exceed 10 cm^{-1} . *cis*-Crotonitrile absorbs at 2226 cm^{-1} and the *trans* isomer absorbs at 2235 cm^{-1} . In older papers the difference is considered to be 3 cm^{-1} (*cis*, 2217 and *trans*, 2220 cm^{-1}) [147].

α, β -Unsaturated nitriles with the two CN groups attached to the same carbon atom show some special features. The $\nu\text{C}\equiv\text{N}$ frequency is higher and the $\nu\text{C}=\text{C}$ frequency is lower. This can be seen by comparing the two nitriles (561) and (562).



(561)

$\nu\text{CN}, \text{ cm}^{-1}$ 2221
 $\nu\text{C}=\text{C}, \text{ cm}^{-1}$ 1637



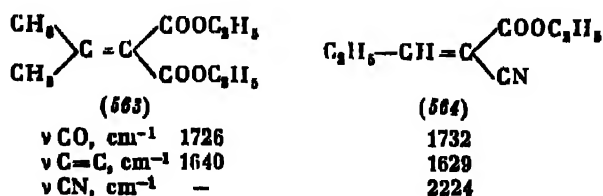
(562)

2234
 1591

In compound (562) the νCN frequency is 13 cm^{-1} higher than in compound (561). These shifts have been attributed to the fact that the two CN groups are not conjugated with each other, but both are conjugated with the $\text{C}=\text{C}$ double bond. Since the electrons of the double bond are withdrawn by both CN groups, the effect on each CN group is small, while the $\nu\text{C}=\text{C}$ frequency decreases appreciably (by 46 cm^{-1}).

In ester-nitriles the νCO frequency increases by approximately 6 cm^{-1} and the νCN frequency decreases by ca. 10 cm^{-1} . The $\nu\text{C}=\text{C}$ frequency has an intermediate value. In these structures the two groups compete for conjugation with the $\text{C}=\text{C}$ bond, which explains the observed variations in frequency

[compare (562) with (563) and (564)]; the νCO frequency in α , β -unsaturated esters is 1720 cm^{-1} .



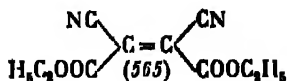
The intensity of the strongly polarized $\nu\text{C}=\text{C}$ band is very high.

In 1, 2-dinitriles the groups attached to the ends of the $\text{C}=\text{C}$ bond tend to polarize it in opposite directions and the carbon atoms of the double bond become more positive. The CN frequency increases by an amount comparable with that in disubstituted 1, 1-dicyano-compounds. In *trans* isomers, for example fumaronitrile, the frequency is 2210 cm^{-1} (the double bond absorption at 1612 cm^{-1} is very weak because of molecular symmetry). In *cis*-isomers the frequency is ca. 10 cm^{-1} lower than in *trans*-isomers [147]. Maleodinitrile absorbs at 2231 and 2251 cm^{-1} (Table II-206). Differences of the same order of magnitude have been observed in methyl-, phenyl-, and dimethylmaleo and fumarodinitriles. In the case of *cis*-isomers, the band is sometimes split and shifts are hidden [38].

Table II-206 Frequencies in α,β -unsaturated nitriles (cm^{-1}) [38]

| Compound | $\nu\text{C}=\text{N}$ | $\nu\text{C}=\text{C}$ | $\nu\text{C}=\text{O}$ |
|-----------------------------|------------------------|------------------------|------------------------|
| Acrylonitrile | 2231 | 1647, 1610 | |
| Crotonitrile | 2228 | 1638 | |
| Metacrylonitrile | 2229 | 1626 | |
| Fumarodinitrile | 2240 | 1612 | |
| Maleodinitrile | 2251, 2231 | 1630, 1599 | |
| Dimethylfumarodinitrile | 2231 | 1615, 1615 | |
| Dimethylmaleodinitrile | 2224 | 1614 | |
| Phenylfumarodinitrile | 2234 | 1592 | |
| Phenylmaleodinitrile | 2225 | 1590 | |
| Methylphenylfumarodinitrile | 2220 | 1593 | |
| Methylphenylmaleodinitrile | 2226 | 1593 | |
| Dicyanodiacethoxy ethylene | 2229 | (1600) | 1750 |

Dicyanodiacethoxyethylene (565) is a special case. The two COOC_2H_5 groups, with a weaker $-I$ effect than the CN groups, are forced to be nonplanar due to steric repulsion. The double bond is conjugated only with the CN groups. The νCO frequency occurs at 1750 cm^{-1} , only 5 cm^{-1} lower than in saturated esters, whereas the CN frequency occurs at 2229 cm^{-1} , 30 cm^{-1} lower than in saturated nitriles. The intensity of the $\nu\text{C}=\text{C}$ band (1600 cm^{-1}) is low ($\epsilon_{\text{max}}^{(a)} = 6$) because of molecular symmetry [38].



$\nu\text{C}-\text{C}$ vibration in α, β -unsaturated nitriles. The weaker double bond character of the $\text{C}=\text{C}$ linkage due to conjugation with the CN group results in a decrease in $\nu\text{C}=\text{C}$ frequency (Table II-206).

This absorption is very strong in asymmetrically substituted compounds because of the high polarity of the bond (induced by the two electron-attracting groups with a strong $-I$ effect).

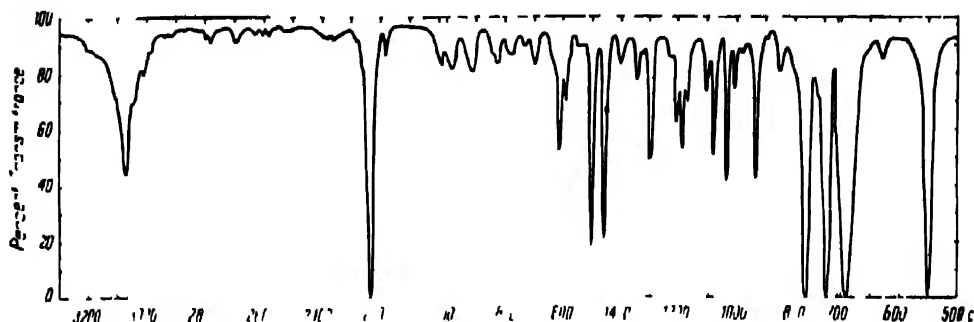


Fig. II-102. Infrared spectrum of benzonitrile.

In symmetrically disubstituted compounds (e. g. in fumaro- and maleo-dinitriles) the effects of the two CN groups on the $\text{C}=\text{C}$ bond are opposite and the intensity of the band decreases appreciably.

d. Aromatic nitriles. In aromatic nitriles the νCN frequency decreases by ca. 20 cm^{-1} , cf. saturated compounds (Fig. II-102).

Frequencies of some aromatic nitriles are shown in Table II-207.

Table II-207 νCN frequencies in nitriles

| Compound | $\nu\text{CN}, \text{cm}^{-1}$ |
|-------------------------------|--------------------------------|
| Alkyl nitriles | 2250 |
| Phenylacetonitrile | 2251 |
| Benzonitrile | 2220 |
| <i>o</i> -Tolunitrile | 2226 |
| <i>m</i> -Tolunitrile | 2229 |
| <i>p</i> -Tolunitrile | 2229 |
| <i>p</i> -Methoxybenzonitrile | 2226 |
| α -Naphthonitrile | 2222 |
| β -Naphthonitrile | 2227 |

Table II-208 Absolute intensities of νCN absorptions in nitriles

| Nitrile | $A \cdot 10^3$ |
|---|----------------|
| CH_3CN | 2.1 |
| $\text{CH}_3\text{CH}_2\text{CN}$ | 2.4 |
| $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$ | 2.5 |
| $\text{C}_6\text{H}_5\text{CN}$ | 4.1 |
| <i>o</i> - $\text{CH}_3-\text{C}_6\text{H}_4-\text{CN}$ | 7.6 |
| <i>m</i> - $\text{CH}_3-\text{C}_6\text{H}_4-\text{CN}$ | 7.7 |
| <i>p</i> - $\text{CH}_3-\text{C}_6\text{H}_4-\text{CN}$ | 10.2 |
| <i>p</i> - $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CN}$ | 18.4 |
| $\text{C}_6\text{H}_7\text{CN}$ | 7.4 |
| $\text{CH}_2=\text{CH}-\text{N}$ | 2.0 |
| $\text{CH}_2=\text{CH}-\text{CH}_2\text{CN}$ | 2.2 |

The intensity of the $\nu\text{C}\equiv\text{N}$ absorption shows large variations in various classes of nitriles. Aliphatic nitriles have higher νCN frequencies and lower intensities. The reverse is true in aromatic nitriles [150, 152, 154].

Absolute intensities A of some aromatic and aliphatic nitriles are shown in Table II-208.

The intensity and frequency of the νCN absorption in aromatic nitriles is related to the Hammett- σ constant of substituents.

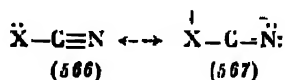
Electron-donating substituents ($-\text{OCH}_3$, $-\text{NH}_2$) give rise to strong bands at low frequencies, whereas electron-attracting substituents ($-\text{NO}_2$) give rise to weak bands at high frequencies [22, 155, 156]. A linear relationship exists between the intensity of the νCN absorption and the resonance energy [150].

c. **Hydrogen bonds.** Nitriles form hydrogen bonds of medium strength with proton donors, such as phenol ($\Delta H = -4$ kcal/mole) and methanol ($\Delta H = -2$ kcal/mole) [157, 158]. Consideration of nitriles as weak bases in a number of papers is due to inadequately chosen examples, where the geometry of the molecule prevents hydrogen bonding $\text{O} \cdots \text{N}$ [159, 160].

In aliphatic nitriles (in CCl_4), there is a linear relationship between $\Delta\nu\text{OH}$ (free νOH — νOH bonded to $\text{N}=\text{C}-\text{R}$) and the Taft inductive constant σ^* of the aliphatic group R . In compounds where R can be conjugated with the CN group, deviations from linearity are observed. They are probably due to resonance between two structures [160]. Some deviations from $\Delta\nu\text{OH}$ values (cm^{-1}) calculated by means of Taft σ^* constants are shown below.

| Phenol + | $\Delta\nu\text{OH}$ obs.— $\Delta\nu\text{OH}$ calc. |
|---|---|
| $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{CN}$ | + 12 cm^{-1} |
| $\text{C}_6\text{H}_5-\text{CN}$ | + 11 |
| $\text{C}_6\text{H}_5-\text{C}\equiv\text{C}-\text{CN}$ | + 10 |
| $\text{CH}_2=\text{CH}=\text{CH}-\text{CN}$ | + 8 |
| $\text{CH}_2=\text{CH}-\text{CN}$ | — 7 |

Large deviations are observed in bromo- and iodoacnide, where structure (567) predominates [160].



The influence of the inductive effect can be seen on comparing $\Delta\nu\text{OH}$ values in compounds shown in Table II-209.

Table II-209 $\Delta\nu\text{OH}$ values on bonding of phenol with $\text{N}-\text{C}-\text{R}$ (0.1 m solution in CCl_4)

| R | $\Delta\nu\text{OH}$ (a) cm^{-1} | R | $\Delta\nu\text{OH}$ (b) cm^{-1} | (a) - (b) |
|-------------------------------|--|-----------------------------|--|-----------|
| $\text{CH}_3(\text{CH}_2)_4-$ | 165* | $\text{Cl}(\text{CH}_2)_4-$ | 165 | 0 |
| $\text{CH}_3(\text{CH}_2)_3-$ | 165 | $\text{Cl}(\text{CH}_2)_3-$ | 158 | 7 |
| $\text{CH}_3(\text{CH}_2)_2-$ | 167 | $\text{Cl}(\text{CH}_2)_2-$ | 148 | 19 |
| CH_3-CH_2- | 165 | ClCH_2- | 117 | 48 |
| CH_3- | 159 | $\text{Br}-$ | 102 | 57 |

Same as in phenol and butyronitrile.

The table shows that replacement of CH_3 by Cl has no effect if the CN group is separated from the chlorine atom by four methylene groups. In the saturated chain the inductive effect decreases with distance.

Shifts depend to a great extent on the concentration of the nitrile. Good results are obtained on extrapolation to infinite dilution [157, 158]. Data in Table II-210 point out large differences between values obtained in neat liquids, in 0.4 m solution of nitrile and phenol in CCl_4 , and at infinite dilution.

Table II-210 νOH frequencies in phenol... nitrile, cm^{-1}

| Phenol + nitrile of | Infinite dilution | 0.4 m Solution in CCl_4 | Neat liquids |
|-----------------------------|-------------------|----------------------------------|--------------|
| Cyclohexane carboxylic acid | 3449 | 3437 | 3406 |
| Pivalic | 3449 | 3442 | 3419 |
| Butyric | — | 3444 | 3408 |
| Acetic | 3461 | 3452 | 3405 |
| Phenylacetic | — | 3453 | 3412 |
| Acrylic | — | 3462 | 3425 |

In dilute carbon tetrachloride solutions α - and β -hydroxynitriles form weak hydrogen bonds. The low shifts in frequency suggest that both the OH group and the π -electrons of the $\text{C}\equiv\text{N}$ group are involved in hydrogen bonding [160].

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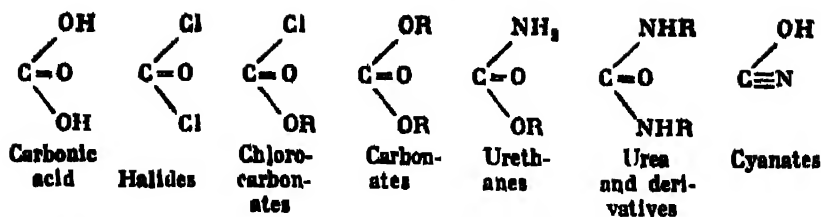
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CHAPTER 9

CARBONIC ACID DERIVATIVES

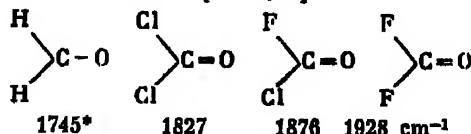
Covalent functional derivatives of carbonic acid are compounds with a central carbon atom linked to two, three, or four atoms other than carbon and hydrogen [1]. They can be derived formally by replacing one or both OH groups in carbonic acid. The most important derivatives are shown below.



Generally monofunctional derivatives are unstable and the majority are unknown in the free state.

1. Carbonic acid halides

Carbonic acid halides have two halogen atoms attached to the carbonyl group. Compared to formaldehyde, replacement of the two hydrogen atoms with electronegative atoms results in a considerable increase in νCO frequency [2-6]*. The largest shifts are produced by fluorine atoms having the strongest $-I$ effect. It should be pointed out that the difference between the COF_2 and COCl_2 absorptions is 100 cm^{-1} [2-4, 6]*.



The high values of these frequencies show that the carbon-oxygen bond order increases from double to triple (the same is observed in the CO group of carboxylic acid halides). It was assumed that contribution of structure (568) is responsible for this effect [5]. Contribution of a polarized structure such as (570) would result in a decrease in frequency. This interpretation is supported by the high frequencies observed in oxocarbenium ions $\text{R}-\text{C}\equiv\text{O}^+$ (see page 224).

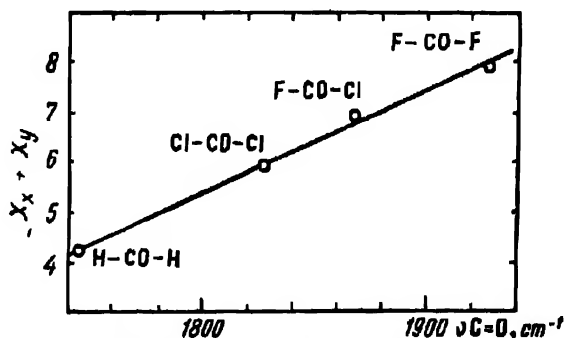
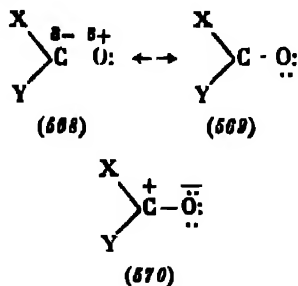


Fig. II-103 Variation of $\nu\text{C}=\text{O}$ frequency with the electronegativity of the halogen atom in YCOX .

A linear relationship has been observed between νCO and the arithmetic sum ($\chi_x + \chi_y$) of the electronegativities of the two halogen atoms (Fig. II-103) [6].

* The reported frequencies vary in different papers.

2. Chlorocarbonates

Chlorocarbonates are characterized by vibrations of C=O, C—O, and C—Cl bonds. The inductive—*I* effect of the chlorine determines the increase in $\nu\text{C=O}$ frequency, the same as in acid chlorides.

In alkyl chloroformates, the mean νCO frequency is $1775 \pm 2 \text{ cm}^{-1}$ [7, 8]. In the liquid phase ethyl chlorocarbonate absorbs at 1776 cm^{-1} [7]. In carbon tetrachloride or carbon disulfide solution the frequency varies by no more than 3 cm^{-1} . The mass of the group R in ClOOR , as well as the presence of a halogen atom in the β -position in the R group, do not affect the frequency very much. However, the presence of a halogen atom in the α -position results in a large increase in νCO frequency (e.g. Cl—COOCCl_3 absorbs at 1806 cm^{-1}) (Table II-211) [7].

Table II-211 Characteristic frequencies (cm^{-1}) in chloroformates (ClOOR (liquid) [7, 8])

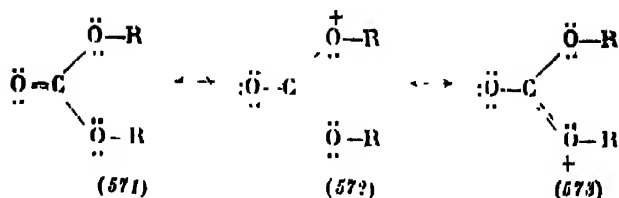
| R | $\nu\text{C=O}$ | $\nu\text{C—O}$ | $\nu\text{C—Cl}$ | $\delta\text{C—Cl}$ |
|---|-----------------|-----------------|------------------|---------------------|
| CH_3 | 1773 | 1147 | — | — |
| C_2H_5 | 1775 | 1160 | 693 | 483 |
| $n\text{-C}_3\text{H}_7$ and $t\text{-C}_3\text{H}_7$ | 1779 | 1156 | 691 | 483 |
| $n\text{-C}_4\text{H}_9$ and $t\text{-C}_4\text{H}_9$ | 1776 | 1145 | 691 | 478 |
| Alkyl ($\text{C}_3\text{—C}_6$) | 1773 | 1168 | 693 | 478 |
| Alkyl (C_{12}) | 1789 | 1160 | 692 | 480 |
| $\text{CH}_3\text{—CH—CH}_3$ | 1799 | 1161 | 693 | 483 |
| $\text{CH}_3\text{—C}_6\text{H}_5$ | 1781 | 1131 | 689 | 471 |
| CCl_3 | 1806 | 1056 | — | — |

The $\nu\text{C—O}$ vibration in chlorocarbonates gives rise to a strong absorption between 1134 and 1172 cm^{-1} [7, 8]. In alkyl chlorocarbonates, the frequency lies in the range $1145\text{—}1168 \text{ cm}^{-1}$. In trichloromethylchloroformate replacement of the three hydrogen atoms of the methyl group by chlorine atoms results in a decrease in frequency to 1056 cm^{-1} (ClCOOCH_3 , 1147 and ClCOOCCl_3 , 1056 cm^{-1}) [7]. It should be pointed out that the majority of chloroformates show two bands between 1050 and 1200 cm^{-1} . Methyl chloroformate (liquid) absorbs at 1147 cm^{-1} (strong) and at 1200 cm^{-1} (medium). In ethyl chloroformate (liquid), the two bands (1140 and 1160 cm^{-1}) are of equal intensity. The assignment of the strong band to a $\nu\text{C—O}$ vibration [9, 10] is supported by other authors as well [7, 8]. The origin of the second band is not clear.

C—Cl vibrations. The stretching vibration of the C—Cl bond occurs at ca. 690 cm^{-1} . Its deformation vibration lies in the range $170\text{—}480 \text{ cm}^{-1}$ [8] (Table II-211).

3. Carbonates

In esters of carbonic acid, the C=O group is attached to two oxygen atoms (571). In these compounds conjugation is stronger than the—*I* effect of oxygen atoms, increasing the contribution of the equivalent structures (572) and (573).

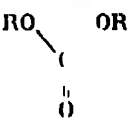
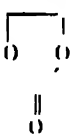
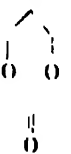



In alkyl carbonates, the $\nu\text{C}=\text{O}$ stretching vibration occurs at $1740\text{--}1760\text{ cm}^{-1}$ close to that of alkyl esters [7, 11]. Dimethyl carbonate absorbs (in CCl_4) at 1755 cm^{-1} [7], and diethyl carbonate (in the same solvent), at 1746 cm^{-1} [11–13]. The frequency increases in unsaturated or aromatic compounds, the same as in esters of carboxylic acids with vinyl or aromatic alcohols. Diphenyl carbonate absorbs at 1775 cm^{-1} . This is explained by the larger contribution of structure (571) where the nonbonded electrons of oxygen are involved in conjugation with the benzene ring. The presence of one or several halogen atoms in the group R raises the frequency by about 40 cm^{-1} . Ethyl trichloromethyl carbonate absorbs at 1780 cm^{-1} , and di-trichloromethyl carbonate, at 1832 cm^{-1} (this frequency is comparable to that of carbonic acid halides) [7].

In cyclic carbonates variations of the $\nu\text{C}=\text{O}$ frequency are similar to those in cyclic functional derivatives of carboxylic acids (anhydrides, lactones, etc.). The frequency varies with ring size. This was attributed to changes in hybridization as a result of ring strain [11–14].

νCO shifts, cf. acyclic analogs, vary with ring size [12, 13]. The highest frequency is observed in five-membered ring carbonates (Table II-212). Chlorine atoms in the α -position to oxygen further increase the $\nu\text{C}=\text{O}$ frequency in five-membered ring carbonates [7]. In strain-free six-membered ring carbonates the increase in frequency is smaller (Table II-212).

Table II 212 νCO frequency (cm^{-1}) in acyclic and cyclic carbonates*

| |  |  |  |  |
|----------------------------|---|---|---|--|
| Liquid | 1742 | 1798 (+56) | 1747 (+15) | 1830 (+88) |
| Solution in CCl_4 | 1746 | 1817 (+71) | 1777 (+31) | 1832 (+90) |

* Values in parentheses are $\Delta\nu\text{CO}$ (νCO cyclic – νCO acyclic).

The majority of carbonates show two νCO bands. The frequency of these bands (Table II-213) varies with experimental conditions (solution, liquid, or solid state) [7]. For instance, ethylene carbonate in the liquid state shows a strong band at 1798 cm^{-1} with a shoulder at 1770 cm^{-1} . In the solid state

the band occurs at 1788 cm^{-1} with a stronger shoulder at 1762 cm^{-1} . In carbon tetrachloride or carbon disulfide solution, the absorption occurs at 1817 cm^{-1} with a shoulder at 1763 cm^{-1} . The effect is stronger in unsaturated carbonates which in CCl_4 have a strong absorption at 1832 cm^{-1} and weak absorptions at 1770 and 1802 cm^{-1} . At higher concentrations the 1802 cm^{-1} absorption becomes stronger. In the liquid state the band occurs at 1830 cm^{-1} with a marked shoulder at 1801 cm^{-1} . In the solid state the band occurs at 1822 cm^{-1} with a shoulder at 1796 cm^{-1} . Propene carbonate does not show the doublet.

Table II-213 Characteristic frequencies (cm^{-1}) in carbonates

| Compound | $\nu\text{C}=\text{O}$ | | $\nu\text{C}-\text{O}$ | References |
|--|------------------------|----------------------------|------------------------|------------|
| | Neat liquid | Solution in CCl_4 | (strongest band) | |
| $\begin{array}{c} \text{OCH}_3 \\ \diagup \\ \text{C}=\text{O} \\ \diagdown \\ \text{OCH}_3 \end{array}$ | 1718 | 1755 | 1280 | [7] |
| $\begin{array}{c} \text{OC}_2\text{H}_5 \\ \diagup \\ \text{C}=\text{O} \\ \diagdown \\ \text{OC}_2\text{H}_5 \end{array}$ | 1742 | 1746 | 1262 | [12, 13] |
| $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{O} \end{array}$ | 1798 1770* | 1817 1763 | 1077 | [7] |
| $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{O} \end{array}$ | 1747 | 1777 | — | [12] |
| $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{O} \end{array}$ | 1830 1801* | 1832 (1770, 1802)** | 1160, 1089 | [7] |

* Shoulder.



** Weak bands.

1. $\nu\text{C}-\text{O}$ vibration. All carbonates show strong bands between 1050 and 1250 cm^{-1} assigned to vibrations of the $\text{C}-\text{O}$ bond [11, 13]. In open-chain compounds the strongest band in this region occurs at ca. 1260 cm^{-1} . Cyclic carbonates show two bands of comparable intensity, between 1070 and 1160 cm^{-1} .

2. Vibrations of CH_2 groups. The vibrational behavior of CH_2 groups in cyclic carbonates is similar to that in cycloalkanes. The frequency increases

by 10–40 cm^{-1} in the five-membered ring, cf. the six-membered ring (Table II-214).

Table II-214 νCH_2 frequencies (cm^{-1}) in cyclic carbonates [12]

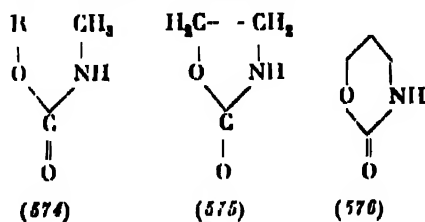
| Compound | νCH_2 (in CCl_4) | | $\Delta\nu = \nu\text{CH}_2 \text{ asym} - \nu\text{CH}_2 \text{ sym}$ |
|---|---------------------------------------|-----------|--|
| | asymmetric | symmetric | |
|  (5) | 3002 <i>m</i> | 2921 | 81 |
|  (6) | 2964 <i>s</i> | 2907 | 62 |

4. Urethanes

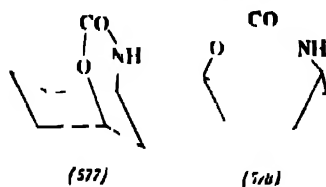
Esters of carbamic acid contain an NH_2 group and an OR group (R =aliphatic or aromatic group) attached to the CO group. The greater involvement of nonbonded electrons of nitrogen in conjugation, cf. oxygen, results in a decrease in the $\text{C}=\text{O}$ bond order.

The νCO frequency varies with physical state. In cyclic urethanes the frequency of five-membered rings is higher, the same as in other cyclic derivatives of carbonic acid (see Carbonates).

In the liquid state *N*-methylurethane (574) absorbs at 1703 cm^{-1} [13], and in dilute carbon tetrachloride solution, the absorption occurs at 1731 cm^{-1} [12]. In five-membered ring cyclic urethanes the frequency increases by ca. 21 cm^{-1} , cf. acyclic analogs [13]. Oxazolidone (575) in the solid state (KBr) absorbs at 1724 cm^{-1} (according to [12], at 1730 cm^{-1}).

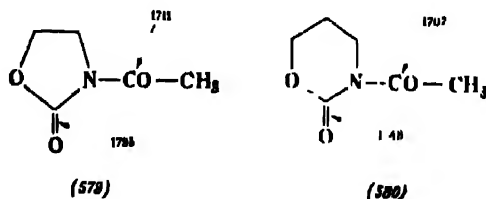


In solution the band shifts toward higher frequencies: 1783 cm^{-1} in carbon tetrachloride and 1760 cm^{-1} in chloroform. Tetrahydrooxazimone (577) absorbs at 1699 cm^{-1} in KBr and 1743 cm^{-1} in CCl_4 [12].



In bicyclic compounds (577) (six- and eight-membered rings) and (578) (two seven-membered rings) in carbon tetrachloride solution, the frequency is 1725 and 1717 cm^{-1} , respectively.

N-Acetylurethanes show two CO bands. *N*-Acetyloxazolidone (579) in the solid state absorbs at 1779 and 1698 cm^{-1} . In solution the frequencies increase to 1795 and 1711 cm^{-1} . In *N*-acetyltetrahydrooxazinone (580), the ν_{CO} frequency of the acetyl group is 1707 cm^{-1} and that of the urethane radical, 1748 cm^{-1} [12].



The N—H stretching vibrations occur in the region characteristic of amides. *N*-Methylurethane absorbs at 3469 cm^{-1} (free N—H) and oxazolidone (575) at 3478 cm^{-1} (free N—H, in CCl_4), and at 3250 cm^{-1} (bonded N—H, in CCl_4). In the spectrum of tetrahydrooxazinone (576) the bands occur at 3454 and 3246 cm^{-1} [12].

5. Urea and its substituted derivatives

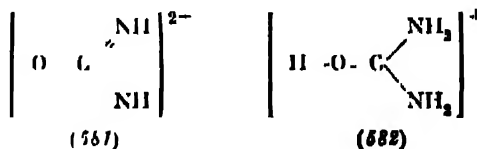
Spectra of urea [15–17] and its substituted derivatives [18] show characteristic patterns of primary, secondary, or tertiary amides of carboxylic acids. In many instances exact assignments of absorption are difficult to make, but the bands have nearly the same properties as in amides [18]. Table II-215 shows characteristic frequencies in urea, *N*-methylurea, and *O*-methylurea [19, 21].

Table II-215 Characteristic frequencies (cm^{-1}) in urea and derivatives

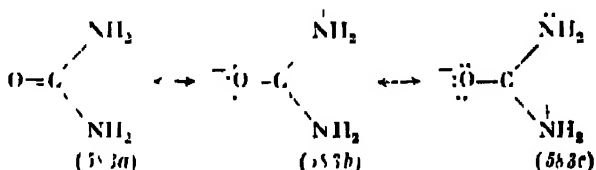
| $\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{C}-\text{NH}_2 \end{array}$ | | $\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{C}-\text{NHR} \end{array}$ | | $\begin{array}{c} \text{OR} \\ \\ \text{H}_2\text{N}-\text{C}-\text{NH}_2 \end{array}$ | |
|---|--|--|--|--|------------------------------|
| 3455 s | | 3435 s | | 3450–3465 m | |
| 3350 s | ν_{NH} | 3330 s | ν_{NH} | 3225–3235 s | ν_{NH} |
| 3285 | | 3220* | | 3170–3180 s | |
| 1687 m | ν_{CO} | 1618 s | $\nu_{\text{C}=\text{O}}$ | 1650–1654 | $\nu_{\text{C}=\text{N}}$ |
| 1627 s | $\nu_{\text{CO}} + \delta_{\text{NH}}$ | | | 1600–1610 | $\delta_{\text{N}-\text{H}}$ |
| 1600 s | | 1578 vs | $(\nu_{\text{CO}} + \delta_{\text{NH}})$ | | |
| 1465 s | | 1420 m | (CN and C—NH ₂) | 1339–1461 ms | (CN and C—NH ₂) |
| 1465 s | C—N | | | | |
| 1155 m | γ_{NH_2} | | | | |
| 1055 w | δ_{NH_2} w | | | | |
| 1000 w | $\nu_{\text{C}-\text{N}}$ | | | | |
| 790 w | (CO + NH) w | | | | |

* Shoulder.

In the urea anion (581), polarization of the C—O bond is favored, the same as in the carbonate ion [15]. In cation (582), the proton can be attached to oxygen or to nitrogen. The infrared spectrum of (582), analogous to that of the isoelectronic guanidinium ion, favors the oxonium structure [22].

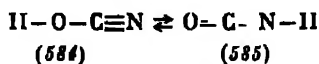


Adducts of urea with saturated straight-chain hydrocarbons, alcohols, halides, etc. have been studied extensively with regard to the nature of bonds in these compounds. The shift of the ν_{CO} band (1687 cm^{-1}) toward lower frequencies ($1649\text{--}1655 \text{ cm}^{-1}$) in adducts of *O*-alkylisourea supports the contribution of polarized structures (583 b, c.) [21].



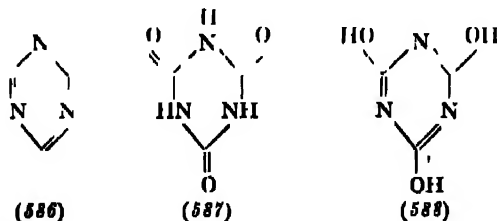
6. Cyanic and isocyanic acid derivatives

The nitrile of carbonic acid, cyanic acid (584) and its tautomeric form, isocyanic acid (585) have not been isolated in the free state. However, some of their derivatives are known [23].



Cyanic acid and its *O*-alkyl derivatives, alkyl cyanates, isolated as trimers (cyanuric acid and derivatives), are special cyclic systems.

Esters and amines of cyanuric acid (melamines) contain the heterocyclic ring of sym triazine (586) and show characteristic frequencies of this system [24].



Structures (587) and (588) have been considered for cyanuric acid. The infrared spectrum shows features supporting structure (587). The amidic $\text{C}=\text{O}$

group has a strong absorption at 1710 cm^{-1} with a shoulder at 1800 cm^{-1} . The $\nu\text{N}-\text{H}$ frequencies are 3210 and 3060 cm^{-1} [25].

1. *Isocyanates*. The esters of isocyanic acid $\text{O}=\text{C}=\text{N}-\text{R}$ have cumulated double bonds. This system shows a strong absorption at ca. 2270 cm^{-1} assigned to the asymmetric vibration of the $\text{N}=\text{C}=\text{O}$ group [26-30]. The band can be readily distinguished from that of nitriles, being almost a hundred

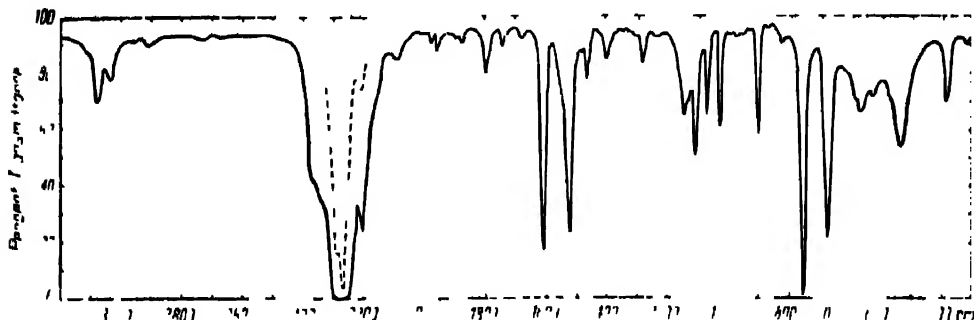


Fig. II-104 Infrared spectrum of phenylisocyanate.

times stronger. Contrary to other isocyanates, phenyl isocyanate $\text{C}_6\text{H}_5-\text{N}=\text{C}=\text{O}$ has a doublet at $2260-2278\text{ cm}^{-1}$ (Fig. II-104).

The band is extremely constant in position. It is not affected by conjugation. Both alkyl and aryl isocyanates absorb within the same limits.

Characteristic frequencies of some isocyanates are shown in Table II-216.

Table II-216 Characteristic absorptions in isocyanates

| Isocyanate | $\nu\text{N}=\text{C}=\text{O}$ cm^{-1} |
|--------------------------------|---|
| <i>n</i> -Butyl | 2273 |
| Isobutyl | 2262 |
| <i>n</i> -Amyl | 2272 |
| Cyclohexyl | 2257 |
| Phenyl | 2260 |
| <i>p</i> -Chlorophenyl | 2262 |
| <i>p</i> -Nitrophenyl | 2262 |
| <i>o</i> -Tolyl | 2273 |
| <i>m</i> - and <i>p</i> -Tolyl | 2268 |
| <i>p</i> -Ethoxyphenyl | 2275 |
| Benzyl | 2268 |

The symmetric vibration band occurring in some isocyanates at $1350-1370\text{ cm}^{-1}$ is weak and, consequently, less characteristic.

2. *Carbodiimides*. Cyanamide derivatives have a cumulated double bond system $\text{R}-\text{N}=\text{C}=\text{N}-\text{R}$. In compounds where R is an alkane or cycloalkane group, the asymmetric $\text{N}=\text{C}=\text{N}$ vibration has a very strong absorption at $2130-2140\text{ cm}^{-1}$. When R is aromatic, the band occurs at $2115-2145\text{ cm}^{-1}$ [31].

The symmetric vibration has a frequency of ca. 1350 cm^{-1} [32].

7. Thiocyanic and isothiocyanic derivatives

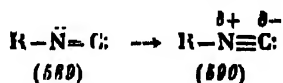
As in the case of cyanic acid, thiocyanic acid and its tautomer isothiocyanic acid ($\text{H}-\text{S}-\text{C}\equiv\text{N}$ and $\text{S}=\text{C}=\text{NH}$) have not been isolated. However, their derivatives are known.

1. *Thiocyanates*. $R-S-C\equiv N$ have a strong absorption in the 2140–2175 cm^{-1} region. Aliphatic thiocyanates absorb at the lower limit (ca. 2140 cm^{-1}) and aromatic cyanates, at the upper limit of the region (2160–2175 cm^{-1}) [33–35].

2. *Aliphatic isothiocyanates*. $R-N=C=S$ have a strong band between 1990 and 2140 cm^{-1} and aromatic isothiocyanates, between 2040 and 2130 cm^{-1} . Often the bands are split or have shoulders. Another characteristic absorption occurs at 1090 cm^{-1} in aliphatic isothiocyanates and at 930 cm^{-1} in aromatic ones.

8. Isonitriles

Isonitriles or carbylamines have the organic group R attached to nitrogen. The nature of the nitrogen–carbon bond in the NC group is that of a resonance hybrid between structure (589), where the carbon atom has an unoccupied orbital, and structure (590) with a triple bond $C\equiv N$ in which the free orbital at carbon is occupied by the unshared electrons of nitrogen [36]



The negative character of the carbon atom in the NC group is supported by dipole moment measurements showing that the negative pole of the vector is at carbon, opposite to the CN group in nitriles.

The C–N bond order corresponds to a state intermediate between the two extreme structures. The electron distribution is largely shifted toward (590) [37–40].

The nature of the group R can increase (+I effect) or decrease the N–C bond order (–I effect) by favoring one of the two structures.

The frequency of the NC group lies in the triple bond region, between 2100 and 2200 cm^{-1} which shows that structure (590) has a large contribution. Because of the polarity of the group, absorptions are very strong.

N \equiv C vibration. Isonitriles have a strong band in the triple bond region, between 2123 and 2183 cm^{-1} [41] (Fig. II-105).

Alkylisonitriles have higher frequencies (2110–2183 cm^{-1}) [12, 13] (Table II-217).

The frequency decreases slightly in the homologous series, from methyl to butyl isonitriles, because of a mass effect [13].

Aromatic isonitriles absorb at slightly lower frequencies because of a weak conjugative effect. The frequency of the phenylisonitrile band is 2123 cm^{-1} , 28 cm^{-1} lower than in butylisonitrile (2151 cm^{-1}).

Substituents in the para-position of the benzene ring have a negligible effect on the NC frequency [44]. In nonpolar, inert solvents, the ν_{NC} vibration is practically unchanged (Table II-218) [44].

Because of its strong polarity, the intensity of the ν_{NC} absorption is almost twice that of the ν_{CN} absorption. This enables the differentiation between nitriles and isonitriles.

The electron-attracting capacity of isonitriles in hydrogen bonding has been extensively studied in the infrared. The proton acceptor is carbon, not

Table II-215 $\nu_{\text{N}\equiv\text{C}}$ frequencies in isonitriles [43]

| Isonitrile | $\nu_{\text{N}\equiv\text{C}}$, cm^{-1} |
|---------------------------------------|---|
| $\text{CH}_3\text{-NC}$ | 2183 |
| $\text{C}_2\text{H}_5\text{-NC}$ | 2160 |
| $n\text{-C}_4\text{H}_9\text{-NC}$ | 2151 |
| $n\text{-C}_6\text{H}_{13}\text{-NC}$ | 2151 |
| $\text{C}_6\text{H}_5\text{-NC}$ | 2123 |

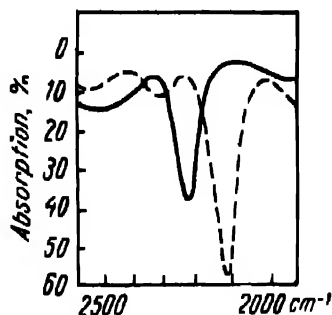


Fig. II-105 The 2000–2500 cm^{-1} region of the ν_{CN} vibration. Solid line—nitrile; dotted line—isonitrile.

hydrogen. This confirms the contribution of structure (590) where the carbon atom has a negative polarity [45, 46].

The strongly basic carbon atom in $\text{C}_6\text{H}_5\text{CH}_2\text{NC}$ forms hydrogen bonds with other donors as well (e. g. with phenylacetylene), the acetylenic

Table II-216 ν_{NC} frequencies of isonitriles in various solvents

| Compound | CHCl_3 | CCl_4 | $n\text{-C}_6\text{H}_{14}$ | CS_2 |
|---|-----------------|----------------|-----------------------------|---------------|
| $\text{C}_6\text{H}_5\text{-NC}$ | 2136 | 2133 | 2134 | 2130 |
| $p\text{-ClC}_6\text{H}_4\text{-C}_6\text{H}_4\text{-NC}$ | 2136 | 2131 | 2132 | 2129 |
| $p\text{-Cl-C}_6\text{H}_4\text{-NC}$ | 2136 | 2133 | 2132 | 2129 |
| $p\text{-CH}_3\text{O-C}_6\text{H}_4\text{-NC}$ | 2140 | 2128 | 2126 | 2124 |
| $\text{CH}_3\text{-NC}$ | 2142 | 2169 | 2168 | — |

ν_{CH} frequency decreases by 30 cm^{-1} in benzylisonitrile solution. In a carbon tetrachloride solution containing phenylacetylene and isonitrile, the acetylenic ν_{CH} band (normally at 3311 cm^{-1}) occurs 30 cm^{-1} lower, as a shoulder on the ν_{NC} band. This indicates the existence of a mixture containing bonded C-H linkages.

It should be pointed out that a larger shift in frequency in isonitriles does not necessarily mean a stronger hydrogen bond, as is the case in alcohols [45, 47].

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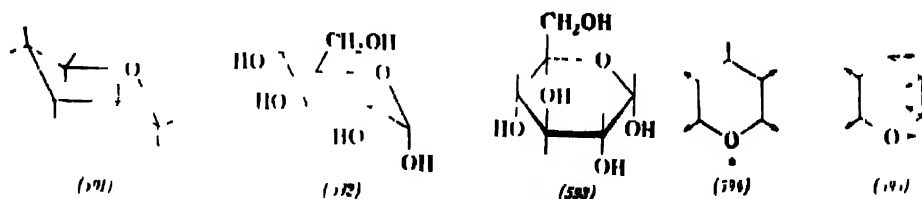
CHAPTER 10

CARBOHYDRATES

Infrared spectra of carbohydrates, even of simple ones, are very complex.

The interpretation of these spectra is based on studies of the spectrum of tetrahydropyran (591) which can be considered the fundamental heterocyclic system in many ketoses (e. g. α -D-glucose (592), (593)) [1].

The spectrum of tetrahydropyran [2, 3a] has been interpreted by analogy with the chair form of cyclohexane. The symmetric vibration (pulsation) of the ring (594) was assigned a frequency of 813 cm^{-1} , and the deformation vibration of the ring (595) was assigned a frequency of 875 cm^{-1} .

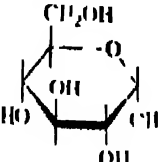
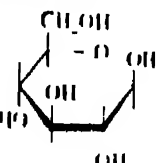


For the characterization of carbohydrates, bands occurring in the 730 – 960 cm^{-1} are being used. They are correlated with the ring vibrations of tetrahydropyran and with CH deformation vibrations of hemiacetal bonds [3a]. Higher frequency regions show C–O, C–C, and C–H vibrations which make interpretations much more difficult.

a. **D-Glucopyranose.** D-Glucopyranose and its derivatives were the first carbohydrates to be studied in detail [1, 3–6]. Correlations found for this monosaccharide are applied both to hexapyranoses (galactose, mannose, etc.) and pentapyranoses. Since spectra of enantiomers are identical, results obtained in the D series are valid also in the L series.

The frequencies of the three characteristic vibration modes in D-glucopyranose are shown in Table II-219.

Table II-219 Characteristic frequencies in α and β -D-glucopyranose

| | Band type 1 cm^{-1} | Band type 2, cm^{-1} | | Band type 3 cm^{-1} |
|---|---------------------------------|-------------------------------|-------------|---------------------------------|
| | | a | b | |
| α -D-Glucopyranose | 917 ± 13 | 844 ± 8 | | 766 ± 10 |
|  | | | | |
| β -D-Glucopyranose | 920 ± 5 | | 891 ± 7 | 774 ± 9 |
|  | | | | |

Band type 1 (917 cm^{-1}) has been assigned to the ring vibration [7] corresponding to the asymmetric deformation of the tetrahydropyran ring at 875 cm^{-1} (595) [2].

Band type 3 occurring at 766 cm^{-1} in α -anomers and at 774 cm^{-1} in β -anomers of sugars corresponds to the 813 cm^{-1} band in tetrahydropyran, assigned to the symmetric ring vibration (594).

The frequency of bands type 1 and 3 is characteristic for α -glycosidic linkages in monosaccharides [4]. It is used for the identification of these linkages in oligo- and polysaccharides. Characteristic frequencies of saccharides with pyranose rings are shown in Table II-220.

Table II-220 Frequencies and assignments in sugars with a pyranose ring [2,5,9]

| Frequency, cm^{-1} | Assignment |
|-----------------------------|--|
| 917 ± 13 | Ring asym vibration |
| 970 ± 14 | Ring sym vibration (pulsation) |
| 844 ± 8 | Glycosidic C-II deformation (α -anomer) |
| 891 ± 7 | Glycosidic C-II deformation (β -anomer) |
| 880 ± 8 | Equatorial C-II deformation, nonglycosidic |
| 867 ± 2 | In-plane deformation $\gamma\text{CH}_2\text{r}$ |
| 967 ± 6 | Terminal CH_2 deformation |

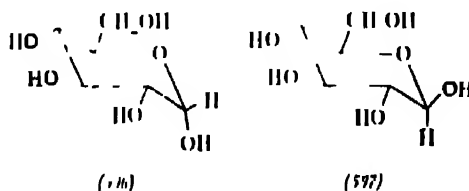
In oligo- and polysaccharides with 1,4- α -glycosidic linkages, a progressive change in frequency of both types of bands is observed (Table II-221).

The frequency of band type 1 increases from 907 (disaccharides) to 930 cm^{-1} (polysaccharides), and the frequency of band 3 decreases from 778 (disaccharide) to 758 cm^{-1} (polysaccharide) [3]. In the polysaccharide Nigerian formed from α -D-glucose residues linked by alternating 1,3 and 1,4 bonds, the frequency is $793 \pm 2 \text{ cm}^{-1}$ (type 3). Dextrane, with α -D-glucose residues linked in the 1- and 6-position has a constant absorption at 917 ± 2 and 768 cm^{-1} . The constant frequency is because no hydroxyl directly attached to the pyranose ring is involved in the glycosidic bond.

Table II-221 Polysaccharides with α -glycosidic bonds

| Bond | Polysaccharide | Type 1 | Type 2 | Type 3 |
|---------------|----------------|-------------|-------------|-------------|
| α -1,4 | Starch | 930 ± 4 | 844 ± 8 | 758 ± 2 |
| α -1,6 | Dextran | 917 ± 2 | 844 ± 8 | 768 ± 1 |
| α 1,3 | Nigerian | | 844 ± 8 | 793 ± 2 |

Band type 2 is assigned to the deformation vibration of the CH bond at the glycosidic carbon atom (position 1). With respect to this band, differences between spectra of mono- and poly-saccharides are small. The absorption enables the differentiation between α - and β -anomers, which can belong either to type 2a or 2b (Table II-219). In D-glucopyranose the α -anomer has a frequency of 811 cm^{-1} and the β -anomer, 891 cm^{-1} . The two anomers differ by the configuration of the glycosidic hydroxyl, consequently by that of the hydrogen attached to the respective carbon atom. In the chair form of the α -anomer of D-glucopyranose this hydrogen atom is equatorial (596) and the glycosidic hydroxyl is axial. In the β -anomer the hydrogen is axial and the glycosidic hydroxyl equatorial (597).



In β -anomers the axial hydrogen atom in the 1-position is sterically close to the axial hydrogen in the 5-position. Appreciable van der Waals forces arise between these two atoms (1,3 interactions in a six-membered ring) resulting in an increase in C—H frequency in β -D-glucopyranose. The same phenomenon occurs in β -D-galactopyranose and in β -D-mannopyranose [1]. However, it has been observed that in α - and β -D-talopyranose each anomer shows

type 2 bands arising both from the α -form and the β -form. This was attributed to the presence of two conformational isomers in both forms [8]. Because some type 1 bands are shifted toward the type 2 band region, assignments of conformations in anomers solely on the basis of these absorptions are not reliable.

Derivatives of D-galactopyranose and D-mannopyranose show a third absorption, type 2c, at 875 cm^{-1} . These monosaccharides differ from glucose by the configuration of atoms C_4 and C_2 , respectively. Consequently, α -anomers have one extra equatorial C—H band [5]. It was assigned the frequency of 875 cm^{-1} (In inositol the equatorial CH groups have frequencies below 875 cm^{-1} , and the axial CH groups have absorptions above 890 cm^{-1} [9].

b. **Desoxy sugars.** The CH_2 group in the pyranose ring gives rise to an absorption at 867 cm^{-1} [9]. This absorption also occurs in 4, 6-O-benzylidene derivatives of α -D-glucopyranoside, at 877 cm^{-1} . It is assigned to the CH_2 group at C_6 , attached to the benzylidene group. In inositol and quercitol the frequency is 853 cm^{-1} [9] corresponding to the 856 cm^{-1} vibration in tetrahydropyran [2].

c. **Sugars with furanose rings.** Assignments in these compounds are less reliable [10]. The ring vibration is assigned a frequency of $924 \pm 13\text{ cm}^{-1}$ and the CH deformation, a frequency of $799 \pm 17\text{ cm}^{-1}$. The hydrogen atoms being equivalent, no differentiation between α - and β -anomers is made.

d. **Cellulose and derivatives.** Cellulose and celluloses modified by chemical or physico-mechanical processes have been studied extensively in the infrared [3, 11–16]. Some aspects are mentioned below.

It should be pointed out that all of the spectra have been recorded in the solid state (KBr, suspension in nujol). The most useful frequencies in studies of structure and structural modifications are those of the OH group. For naturally occurring cellulose the frequencies used in practice are shown in Table II-222 [3, 11–13].

Conclusions regarding the degree of crystallinity of the sample, modifications which take place on treatment with various chemical or physical agents, polymorphism etc. can be drawn on the basis of hydrogen bonding studies [3, 13]. In raw cotton the bonded νOH absorption occurs at 3356 cm^{-1} , and in linters the frequency is 3330 cm^{-1} . In chemically modified cotton, the νOH absorption occurs at higher frequencies. In methyl cellulose prepared from linters the absorption occurs at 3401 cm^{-1} , and in ethyl cellulose of the same origin at 3425 cm^{-1} . Cellulose acetate has a still higher frequency, $3497\text{--}3509\text{ cm}^{-1}$, and carboxymethyl cellulose, ca. 3378 cm^{-1} . Cellulose regenerated from acetate has a lower frequency (3400 cm^{-1}), cf. 3490 cm^{-1} in partially acetylated cellulose. These figures have a comparative value; however, the conclusion is drawn that reactions occur in the amorphous region.

Deuteration has shown that in the highly crystalline region a very small change occurs on replacing OH by OD. The intensity of the OH band enables the determination of the ratio of modified OH. Amorphous regions

are easily deuterated. In this way the degree of crystallinity can be established exactly [14].

The orientation of macromolecular chains in oriented fibers can be followed by polarized infrared radiation [15]. The CH_2 deformation band at 1437

Table 11-222 Characteristic frequencies in cellulose [13]

| Frequency, cm^{-1} | Vibration |
|-----------------------------|---|
| 3125–3571 | free νOH and bonded νOH |
| 1631 | H_2O |
| 1437 | Deformation CH_2w |
| 1377 | Deformation CH |
| 1340 | In-plane deformation OH |
| 1319 | Deformation OH or CH_2w |
| 1285 | Deformation OH or CH_2w |
| 1247 | Deformation OH or CH_2w |
| 1161 | Not assigned |
| 1117 | Ibid. |
| 1058 | Ibid. |
| 1030 | Ibid. |
| 829 | Deformation CH_2w |

cm^{-1} becomes stronger when the degree of crystallinity increases. It vanishes on breaking. As a measure of the degree of crystallinity, the ratio of bands $1449/909 \text{ cm}^{-1}$ has also been proposed [12].

Infrared spectra show that on oxidation CH_2OH groups are transformed into COOH groups. Bands occur at ca. 1750 cm^{-1} (COOH). Under certain conditions oxidation leads to CHO and $\text{C}=\text{O}$ groups (hydrated). They can be identified by absorptions at 1721 cm^{-1} [12].

On transformation of cellulose in esters and ethers, the spectra show absorptions of the newly formed functional derivative, while OH absorptions vanish partially or totally [13, 16]. By studying the intensity of these bands, it is possible to follow the modification process [13].

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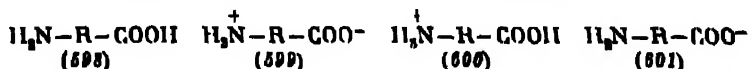
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CHAPTER 11

AMINO ACIDS, PEPTIDES AND PROTEINS

A. AMINO ACIDS

In the crystalline state as well as in solution, amino acids (598) exist at their isoelectric point in the form of zwitterions (599) which result from internal neutralization of the acidic and basic groups in the molecule.

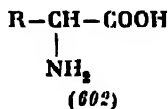


Because of their zwitterionic character, amino acids behave like bases in acidic solutions and like acids in basic solutions. In the former case they occur as cations (600), and in the latter, as anions (601). In neutral aqueous solutions, amino acids exist as species (599), (600), and (601) because of protolytic equilibria with water. The concentration of neutral molecules (598) is so small that they are practically unidentifiable [1].

Because of the structure and behavior of amino acids in solution, their infrared spectra show a complicated pattern strictly dependent on experimental conditions.

For a long time the insolubility of amino acids in common solvents used in infrared spectroscopy has limited the recording of spectra to the solid state (suspension in nujol or KBr). The improvement of techniques using aqueous solutions has made more extensive studies possible.

Studies of amino acids are concerned with research in the protein field. Therefore naturally occurring amino acids obtained by hydrolysis of proteins have been the most extensively studied in the infrared. The common feature in these compounds is primarily the presence of NH_2 group in the α -position to a carboxyl group (602)



The special character of each of the well-known seven groups of naturally occurring amino acids is because of the different nature of the group R [1, 2]. Sometimes this character can be recognised in the infrared spectrum. Neglecting absorptions arising from the group R, the behavior of the two functional groups depends on experimental conditions. In the solid state or in aqueous solution at the isoelectric point, structure (599) is characterized by absorptions of NH_3^+ and COO^- groups. In basic medium or in water soluble salts (structure 601), bands arising from the NH_2 group occur along with those arising from the ion COO^- (the former also occur in diamino acids). Hydrochlorides of amino acids (600) are characterized by NH_3^+ and COOH absorptions. The latter are slightly shifted, due to the presence of the polar NH_3^+ group. Absorptions of the COOH group (dimer) also occur in dicarboxylic acids.

a. Vibrations of the NH_2 group. By analogy with the CH_3 group, the NH_2 group is assigned an asymmetric and a symmetric stretching vibration similar to those of hydrochlorides of primary amines.

According to the above statements, zwitterionic amino acids do not show absorptions in the NH stretching vibration region at 3200 cm^{-1} . They show a broad band between 3030 and 3130 cm^{-1} assigned to the asymmetric stretching vibration of the NH_3^+ group. The absorption of the symmetric vibration is weak and occurs between 2000 and 3000 cm^{-1} [2-6]. It has not been identified in all amino acids. In the majority of cases the bands occur at 2080 – 2140 and 2530 – 2760 cm^{-1} [6]. The absorptions are strictly dependent on the structure of the amino acids. Aspartic acid, for example, shows two bands: 1905 and 2062 cm^{-1} ; lysine absorbs at 2083 and serine at 2033 cm^{-1} [2].

Hydrochlorides of amino acids containing the NH_3^+ group absorb between 3049 and 3145 cm^{-1} . It should be pointed out that this broad band also shows other peaks depending on the structure of the amino acids. The lack of regularity in these maxima is due to associations between molecules of amino acids (in the solid state), resulting in large shifts towards lower frequencies. This makes differentiations between νOH , νNH , and νCH absorptions difficult.

In nitrogen-substituted amino acids the absorptions of the $>\text{NH}_2$ or $>\text{NH}$ groups occur at 2250 – 2700 and 2450 cm^{-1} , respectively (as in hydrochlorides of secondary and tertiary amines) [6].

Deformation vibrations of the $\alpha\text{-NH}_3^+$ group give rise to absorptions between 1500 and 1600 cm^{-1} along with those arising from the ion COO^- . The asymmetric deformation band occurs at 1610 and 1660 cm^{-1} as a shoulder on the broad COO^- band which sometimes covers it. The symmetric deformation band is stronger and occurs at lower frequencies, between 1485 and 1550 cm^{-1} [2, 5, 6-9]. The asymmetric vibration can be observed in racemic compounds, but does not occur in enantiomers [10].

Deformations of the $>\text{NH}_3^+$ group in *N*-substituted amino acids (e.g., sarcosine, proline) occur at 1500-1600 cm^{-1} . The band is covered by the absorption of the COO^- ion.

In hydrochlorides of amino acids (600) which do not contain the carboxylate ion, the two deformation modes of the NH_3^+ group can be readily distinguished. The asymmetric vibration band occurs at 1590-1610 cm^{-1} and the symmetric one, at 1470-1550 cm^{-1} . In *L*-leucine hydrochloride, the frequencies of the two bands are 1590 and 1475 cm^{-1} , respectively [11].

b. **Vibrations of the COO^- group.** In zwitterion (599) and anion (601) the two vibration modes of the carboxylate ion are readily identifiable between 1410 and 1600 cm^{-1} . The asymmetric vibration band is strong and broad (1560-1600 cm^{-1}) [6, 12]. Sometimes it covers the NH_3^+ band. The second band, weaker but narrower, occurs at ca. 1410 cm^{-1} [2]. It is more difficult to identify because of its weakness. In naturally occurring alanine (in KBr) the frequencies of the two bands are 1592 and 1412 cm^{-1} [11]. In solution the COO^- absorption of the zwitterion occurs at 1618 cm^{-1} . In alkaline solution *L*-alanine absorbs at 1570 cm^{-1} [12]. β -Alanine has the same frequency (1618 cm^{-1}) in KBr and in solution.

The variation of absorptions in this region with the structure of the amino acid can be seen by comparing spectra of glycine in D_2O [13]. In neutral solution the COO^- group of (599) absorbs at 1610 and 1400 cm^{-1} . On adding DCl these absorptions are replaced by the absorption of the COOH group at 1740 cm^{-1} (607). In basic medium (NaOH), the absorptions of the carboxylate ion reappear at 1590 and 1400 cm^{-1} .

c. **Vibrations of the COOH group.** The carboxyl band only occurs in hydrochlorides of monocarboxylic α -amino acids. In dicarboxylic amino acids, it occurs along with bands of the zwitterion. In natural α -amino acids, the $\nu\text{C}=\text{O}$ absorption is shifted toward higher frequencies (1724-1754 cm^{-1})

than in amino acids with more remote NH_3^+ groups. The latter have normal absorptions (1700-1730 cm^{-1}); for example, the hydrochloride of δ -aminovaleric acid absorbs at 1711 cm^{-1} . The rise in COOH frequency in α -amino acids is due to the strong $-I$ effect of the quaternary -NH_3^+ group (the effect is similar to that of a halogen atom or electron-withdrawing group such as OH or C=O). The $-I$ effect of the quaternary nitrogen atom also occurs in

N-substituted amino acids. For example, in sarcosine hydrochloride $\text{CH}_3\text{NH}_3^+\text{-CH}_2\text{COOH}$, the $\nu\text{C}=\text{O}$ absorption occurs at 1757 cm^{-1} ; in *N*-phenylglycine and

proline, it occurs at 1730 cm^{-1} ; in ornithine dihydrochloride at 1739 cm^{-1} , and in histidine hydrochloride at 1706 cm^{-1} .

d. **Vibration of the NH_2 group.** Salts of amino acids show, along with bands arising from the COO^- group, absorptions of the NH_2 group between 3300 and 3500 cm^{-1} (at higher frequency than absorptions arising from the NH_2^+ groups at $3030\text{--}3130\text{ cm}^{-1}$). The δNH_2 band in ornithine and lysine occurs at 1515 cm^{-1} . If the two NH_2 groups are in adjacent positions, as in α , β -diaminopropionic acid, the band is split into two components with frequencies of 1546 and 1477 cm^{-1} because of interaction between the two groups. In α , γ -diaminobutyric acid the interaction is weaker and the two bands occur at 1515 (weak) and 1486 cm^{-1} . Histidine shows a similar phenomenon. The band at 1462 cm^{-1} is strong and that at 1499 cm^{-1} is very weak.

e. **Vibrations of the OH group.** The OH group in amino acids is involved in hydrogen bonding, and the band is shifted toward lower frequencies (between 3100 and 3500 cm^{-1}). In general, hydroxyamino acids have a band in the 3300 cm^{-1} region [2].

f. **Vibrations of the group R.** In naturally occurring amino acids, the group R attached to the $-\text{CH}(\text{NH}_2)-\text{COOH}$ residue gives rise to some absorptions which may be useful to identify individual members of the series; for example, monocarboxylic amino acids with an alkyl or isoalkyl chain show CH_2 absorptions at 1370 and 1450 cm^{-1} and CH_3 bands at 1330 cm^{-1} [14, 15]. Obviously, glycine does not show the 1370 cm^{-1} band, and alanine does not absorb at 1330 cm^{-1} . Phenylalanine and tyrosine show the characteristic phenyl band at 1613 cm^{-1} . Tryptophane, with an indole ring, differs from other amino acids by its strong absorption at 1672 cm^{-1} . Spectra of cysteine and cystine are very similar between 1660 and 3330 cm^{-1} . Below 1600 cm^{-1} some characteristic differences are observed [2].

g. **Optical isomers (Enantiomers).** Racemic amino acids and the optically active forms have identical spectra in solution. However, in the solid state some differences do occur [16]. The same differences have also been observed in derivatives of amino acids [17, 18]. Spectra of L-alanine and D-alanine show small differences in the 2985 , 1540 , and 1030 cm^{-1} regions [10, 16]. X-ray studies have shown that the two compounds have similar crystalline lattices.

Spectra of racemic D, L-serine and optically active L-serine are sufficiently different to enable their identification [3].

| | νOH | νNH_2^+ | $\nu\text{COO}^- - \delta\text{NH}_2^+$ |
|------------|----------------|--------------------|---|
| L-serine | 3484 | 3077 | 1600 (broad) |
| D,L-serine | 3630–3125 | | 1670, 1642, 1499 |

These differences have been attributed to different association modes in the two substances. It is assumed that the racemic compound has stronger hydrogen bonds between the hydroxyl group and both the COO^- ion and the

NH_3^+ group. Because of this the spectrum does not show the ordinary vibrations of the OH or NH_3^+ groups. In L-serine and its enantiomer, D-serine, the OH is very little or not at all involved in hydrogen bonding. Spectra of these compounds show the νOH band at ca. 3480 cm^{-1} . These observations are supported by X-ray studies [19]. Other amino acids and peptides show a similar behavior [2, 10, 20]. In contrast with enantiomers, diastereoisomers have different spectra and can be readily distinguished [2].

h. Complex salts of amino acids. Salts of amino acids with transition metals (Cu^{II} , Ni^{II} , Zn^{II} , etc.) have been studied extensively in the infrared in order to determine the nature of the metal-ligand bond [21-25].

The structure of complexes, such as ethylenediaminetetra-acetic acid $(\text{HOOC})_2\text{NCCH}_2-\text{CH}_2\text{N}(\text{COOH})_2$ (EDTA), has been studied in order to determine the ligand function of this compound under various conditions [26]. It has been shown that in hexadentate EDTA all COOH groups are coordinated. The spectrum shows a single absorption at 1650 cm^{-1} (the only absorption in the $1550-1750\text{ cm}^{-1}$ region). In complexes in which EDTA is coordinated by means of two nitrogen atoms and three carboxyl groups, the fourth free carboxyl can be recognized by its absorption at 1750 cm^{-1} occurring along with that at 1650 cm^{-1} [21, 26].

B PEPTIDES AND PROTEINS

Infrared spectra of proteins show broad, strong and non-differentiated bands as a result of their complex structure. The obvious cause is the diversity of amino acids forming the protein molecule. The broad bands are in fact envelopes of bands corresponding to residues of individual amino acids partially or totally superimposed. For this reason the primary structure, i.e. the nature and sequence of amino acid residues can only rarely be studied by infrared spectroscopy. However, investigation of the $\text{NH}-\text{CO}$ vibration region can be very helpful in elucidating some problems concerned with secondary structure. These studies are based on correlations between band shifts and strength of hydrogen bonds, behavior of proteins and polypeptides on deuteration, and dichroism studies in the infrared.

The interpretation of infrared spectra of complex protein molecules is based on work done with simpler peptide molecules, where the nature and sequence of amino acids are established by synthesis. It has been observed that α and β forms of polypeptides show different patterns in their infrared spectra, behave differently on deuteration and show a different dichroism. It is thus possible to follow the polymerization reaction by infrared spectroscopy and determine conditions under which the different forms of peptides, α , β , or random, can be obtained.

a. Characteristic frequencies. The common group in peptides and proteins $-\text{NH}-\text{CO}-$ involves characteristic vibrations of secondary amides,

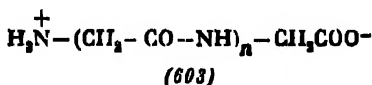
Alterations in normal frequencies occurring in infrared spectra of some *N*-alkylamides in the solid state or in concentrated solution indicate the presence of hydrogen bonds and enables one to gain some knowledge of the mode and degree of association of polypeptide chains.

In the following sections, some characteristic patterns of peptide spectra will be discussed, starting with the simplest ones.

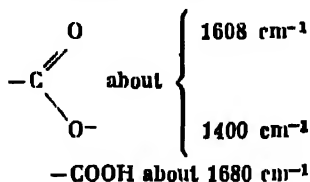
Polyglycine. Early work on simple peptides [27] containing 2–6 glycine residues (di-, tri-, tetra-, and hexaglycine) and on polyglycine [28] has shown an alteration of the spectrum with molecular weight. Glycyl-glycine $\text{H}_2\text{NCH}_2\text{CONHCH}_2\text{COOH}$ containing two amino acid residues still maintains the zwitterionic structure and has a complex spectrum. In higher members of the series, spectra become increasingly similar to each other and to spectra of proteins. Characteristic bands in spectra of solid polyglycines show characteristic frequencies of the peptide linkage $-\text{NH}-\text{CO}-$:

$$\begin{aligned}\nu\text{NH} &\text{ about } 3300 \text{ and } 3080 \text{ cm}^{-1}, \\ \nu\text{C}=\text{O} &\text{ about } 1650 \text{ cm}^{-1}, \\ \delta\text{N}-\text{H} &\text{ about } 1515 \text{ cm}^{-1}.\end{aligned}$$

In addition to these bands encountered in all polyglycines (603), lower members, with 2–4 amino acid residues, show bands arising from the zwitterionic structure [27].



$$\begin{aligned}\nu\text{NH}_2 &\text{ about } 3080 \text{ cm}^{-1}, \\ \delta\text{NH}_2 &\text{ about } 1630 \text{ cm}^{-1}, \\ \delta\text{NH}_2 &\text{ about } 1575 \text{ cm}^{-1},\end{aligned}$$



In low molecular weight polyglycines with a predominantly zwitterionic structure, the carboxyl band at 1680 cm^{-1} occurs as a small shoulder of low intensity. In higher members, the band of the carboxylate ion at 1400 cm^{-1} becomes weaker or vanishes completely while the band arising from the undissociated COOH at 1680 cm^{-1} group is maintained [27, 29]. It should be pointed out that under the same conditions this band does not occur in the spectrum of glycine because of dimerization of the carboxyl [27] (see Acids).

The 3000 cm^{-1} region shows CH_2 bands at 2925 cm^{-1} (νCH_2 *asym*) and 2860 cm^{-1} (νCH_2 *sym*).

The 3300 cm^{-1} band assigned to the bonded N—H linkage shows an increase in intensity with increasing molecular weight.

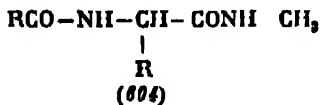
The widely discussed 3080 cm^{-1} band [30] is replaced on deuteration by two bands with frequencies of 2530 and 2480 cm^{-1} corresponding to N—D stretching vibrations [27]. The spectrum of glycylglycine shows a very strong band at 1015 cm^{-1} . It is considered characteristic for the diglycine structure since it does not occur in alanyl-glycine and in other peptides where glycine residues are separated by different amino acids (e.g. polyglycyl-D,L-phenyl-alanine). It does not occur in poly-D,L-alanine or poly-β-alanine, but does arise in some optically active forms of mixed polypeptides [31, 32].

At ca. 700 cm^{-1} polyglycines have a strong band associated with the γCH_2 frequency of the methylene groups. The intensity of this band diminishes on deuteration. It has been tentatively assigned to a contribution by coupling of an NH vibration. The band occurs also in some peptides, polypeptides, and proteins [27]. Differences in spectra of short chain peptides, containing less than five amino-acid residues, and spectra of high molecular weight polypeptides also occur in other representatives. For example, spectra of various low molecular weight poly-γ-benzyl glutamates are different. On lengthening of the polypeptide chain, the spectra become similar. This enables the correlation of the observed differences with α-, β-, or random conformations of chains [28, 33].

Optically active peptides with one or several asymmetric carbon atoms show different patterns in the —NH—CO— vibration region [31].

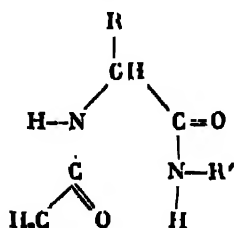
Spectra of enantiomers are identical and differ from those of diastereoisomers; for example, D-glycyl-D-alanine and L-glycyl-L-alanine have identical spectra. These spectra differ from those of D, L and L, D glycyl-alanines, which in turn are identical [31].

Studies of polyglycines paved the way toward the investigation of simpler analogs of peptides and enabled the interpretation of spectra of complex polypeptides and proteins. A large number of *N*-methyl amides (604) of *N*-acyl-*N*-benzoyl-, *N*-carbobenzoxy-, etc., amino acids have been investigated.

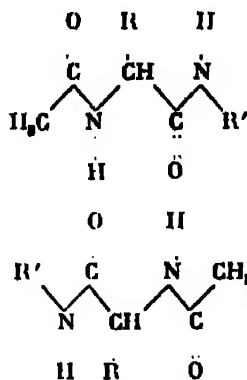


Spectra of these molecules are similar to those of polypeptides both in the 3300 and the $1550 - 1650\text{ cm}^{-1}$ region. Acetyl-glycine-*N*-methylamide $\text{CH}_3\text{CONH-CH}_2\text{-CONHCH}_3$ shows two bands in the N—H stretching vibration region, depending on solvent and concentration [31–36]. In dilute carbon tetrachloride solution, a band occurs at 3330 cm^{-1} assigned to the bonded NH group. Another band occurs at 3450 cm^{-1} and is assigned to the free NH vibration. The 3330 cm^{-1} band was assigned to an NH vibration involved in intramolecular hydrogen bonding with the C=O group of the acetyl residue, characteristic for the folded conformation (605) of polypeptides. The 3450 cm^{-1} band has been assigned to the free NH group in compounds

$\text{CH}_3\text{CONHCHRCONHR}'$ [34, 35] both in the folded conformation (605) and the extended conformation (606).



(605)



(606)

In the extended conformation, the hydrogen bonds are intermolecular. Their frequency is approximately equal to that of intramolecular $-\text{NH}\cdots\text{O}=\text{C}-$ bonds in the folded conformation. Because of this, the νNH band at 3330 cm^{-1} becomes stronger at high concentrations.

In acetylglycyl-*N*-methylamide and acetyl-leucyl-*N*-methylamide the 3448 cm^{-1} band is split into two bands arising at 3160 and 3425 cm^{-1} when the spectra are recorded in very dilute carbon tetrachloride solutions [37] (Figure II-106).

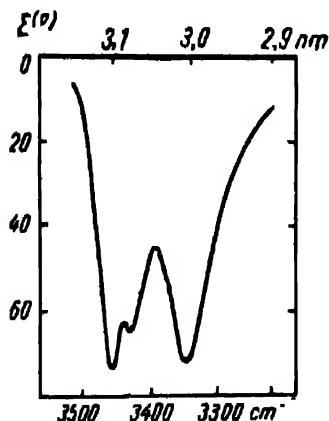


Fig. II-106 Infrared spectrum of acetylglycyl-*N*-methylamide in 0.0002 M carbon tetrachloride solution [37]

In dilute carbon tetrachloride solution, bands arising from the free NH in acetylvaline-*N*-methylamide and acetylnorleucine-*N*-methylamide occur at 3172 and 3425 cm^{-1} , respectively. The band assigned to the bonded NH occurs at 3311 cm^{-1} . At higher concentrations the bonded NH band shifts to 3310 cm^{-1} [37]. In concentrated chloroform solution in which *N*-methyl amides of acetylamino acids are more soluble than in carbon tetrachloride, the spectra show the same bands as in dilute carbon tetrachloride solution: two νNH bands arising from the free NH , at 3172 and 3425 cm^{-1} , and one band arising from the bonded NH , between 3310 and 3311 cm^{-1} . The bonded νNH band of acetylnorleucine in carbon tetrachloride solution is twice as

strong as the free νNH band. In chloroform the latter is hardly visible at a concentration of 0.1 mole/l . This shows that the solvent affects the equilibrium ratio between forms (605) and (606).

In polypeptides, characteristic frequencies of NH and CO groups occur in all possible forms (α , β , and random). The most extensively studied are

bands arising from νCO vibrations (amide I) and from δNH deformation vibrations (amide II). Frequencies of these bands vary with the conformation of the molecule and are used in investigations of secondary structures of proteins and polypeptides [38]. The νNH stretching vibration is less sensitive (see Table II-223).

νCO and δNH frequencies are higher in folded α -forms than in extended β -forms. These frequencies enable the differentiation of chain types in random fibers and are useful in studies of configuration of fibers obtained under diffe-

Table II-223 Characteristic frequencies in polypeptides (cm^{-1})

| Vibration type | α -Form | β -Form | Frequencies of free bonds |
|--------------------------------------|----------------|---------------|---------------------------|
| $\nu\text{C}=\text{O}$ (amide I) | 1650–1660 | 1630 | 1680–1700 |
| $\delta\text{N}-\text{H}$ (amide II) | 1540–1550 | 1520–1525 | <1520 |
| $\nu\text{N}-\text{H}$ | 3200–3300 | 3280–3300 | ca. 3480 |

rent experimental conditions or by different synthetic pathways. In the solid state poly- γ -benzyl-L-glutamate of low molecular weight absorbs at 1630 cm^{-1} , which corresponds to a β -conformation. In dilute chloroform solution the frequency increases to 1660 cm^{-1} and in dioxane to 1680 cm^{-1} . This shift shows that in concentrated solution or in the solid state β -polypeptides form intermolecular associations. The new solvent dependent bands are assigned to solvated forms.

In this way it has been shown that high molecular weight poly-benzyl-L-glutamates (20,000–350,000) exist in the α -form. In the solid state, in chloroform, or in dioxane, the frequency of the νCO band is $1650 \pm 2\text{ cm}^{-1}$ [39].

b. **Dichroism.** Polarized radiation has been used extensively in studies of conformation of polypeptides and proteins.

In order to determine the dichroic ratio of bands the usual reference direction is the axis of the fiber or the stretching direction of the polypeptide film. The bands used in dichroism measurements are those arising from the characteristic vibrations of the $-\text{NH}-\text{CO}-$ group: the νNH stretching vibration at ca. 3330 cm^{-1} , the amide I band (νCO) at ca. 1650 cm^{-1} , and the amide II band (δNH) at ca. 1550 cm^{-1} .

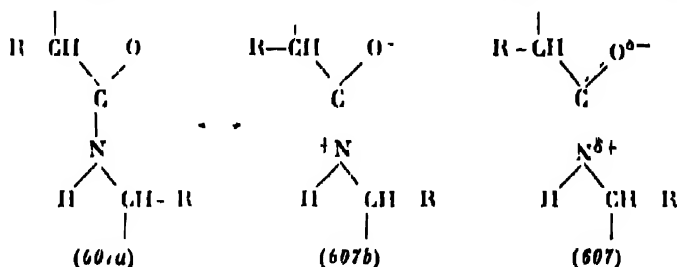
Table II-224 shows the dichroism of characteristic bands of some polypeptides and proteins in oriented films.

Table II-224 Dichroism of characteristic bands in proteins and polypeptides [40]

| α -Forms (folded) | | β -Forms (extended) | | Collagen | | Vibration type |
|--------------------------|-----------|---------------------------|-----------|-----------------------|-----------|----------------------------|
| ν, cm^{-1} | Dichroism | ν, cm^{-1} | Dichroism | ν, cm^{-1} | Dichroism | |
| 3330 | π | 3330 | σ | 3330 | σ | νNH |
| 1660 | π | 1640 | σ | 1660 | σ | νCO |
| 1545 | σ | 1525 | π | 1548 | π | δNH |
| 4830 | σ | 1825 | π | 4865 | π | Overtones and combinations |
| 1600 | — | 4530 | π | 4590 | σ | |

Collagen and β -keratine show perpendicular dichroism for νNH and νCO stretching vibrations and parallel dichroism for δNH bands. This shows that $\text{N}-\text{H}$ and $\text{C}=\text{O}$ groups have an approximately perpendicular orientation with respect to the axis of the fiber [41]. In α -keratine νNH and $\nu\text{C}=\text{O}$ bands show parallel dichroism. The orientation of the respective bands is parallel to the axis of the fiber.

The interpretation of the behavior of polypeptide chains in polarized infrared confirms the folded model proposed by Pauling and Corey [42, 43] for β -forms and the α -helix for α -forms. In the folded model the peptide groups of the fibers are planar because of amidic conjugation between forms (607a) and (607b). CH_2 groups are alternatively out-of-plane on both sides.



Polypeptide chains can be oriented all in one direction (parallel orientation) or in opposite directions (antiparallel orientation) [43].

In α -forms, polypeptide chains have the aspect of a helicoidal staircase where each amino acid residue corresponds to a step. The stability of such a structure is due to hydrogen bonding between $\text{C}=\text{O}$ and NH groups of superimposed coils. Here too, the chains can have a parallel or antiparallel orientation.

In solution, chains can have a random form.

Table II-225 shows calculated and experimental values for frequencies of various forms of polypeptide chains [11].

Table II-225 Frequencies (cm^{-1}) in polypeptides

| Polypeptide form | Dichroism | Amide I band | | Amide II band | |
|---------------------------------------|-----------|---------------|--------------|---------------|--------------|
| | | Observed | Calculated | Observed | Calculated |
| Parallel folded chains | π | 1645 <i>w</i> | 1648 | 1530 <i>s</i> | 1530 |
| | σ | 1630 <i>s</i> | 1632 | 1550 <i>w</i> | 1550 |
| Antiparallel folded chains | π | 1685 <i>w</i> | (1685) | 1530 <i>s</i> | (1530) |
| | σ | 1632 <i>s</i> | 1632 1668 | | 1540 1550 |
| Parallel extended chain (Nylon 66) | | 1610 | 1640 | 1540 <i>s</i> | (1540) |
| α -Helix | π | 1650 <i>s</i> | (1650) | 1516 <i>w</i> | (1516) |
| | σ | 1652 <i>m</i> | 1647 | 1546 <i>s</i> | 1540 |
| Random | | 1656 <i>s</i> | 1658 | 1535 <i>s</i> | 1535 |

1. *Extended forms.* Studies performed on Nylon 66 (Fig. II-107) show that this synthetic polymer containing -NHCO- linkages separated by four or six methylene groups exists in a *completely extended* form with *parallel* chains. Hydrogen bonding occurs between CO and NH groups of neighboring chains. In forms with a high degree of crystallinity, the frequency of the amide I band is 1640 cm^{-1} . The amide II band occurs at 1510 cm^{-1} [41].

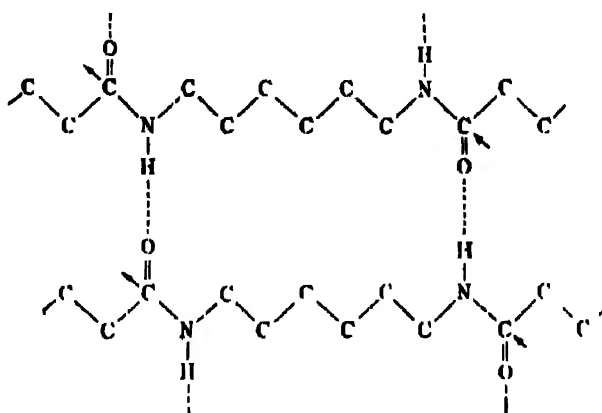


Fig. II-107 Extended chains (Nylon 66).

In *antiparallel layers*, for example, in polyglycine [27, 11], the amide I band is split into a doublet. The component at 1685 cm^{-1} has a weak parallel dichroism and that at 1632 cm^{-1} , a perpendicular dichroism. The splitting of the band ($\Delta\nu = 53\text{ cm}^{-1}$) was attributed to vibrational interactions between chains. The amide II band has a frequency of 1530 cm^{-1} and shows a parallel dichroism.

An example of *parallel folded layers* is β -keratin with two amide I bands, one at 1615 cm^{-1} with parallel dichroism and the other at 1630 cm^{-1} with perpendicular dichroism. This is in agreement with the calculated values of 1618 and 1632 cm^{-1} respectively (Table II-225). The splitting of the amide I band ($\Delta\nu = 15\text{ cm}^{-1}$) is due solely to chain interactions. The amide II band occurs at 1530 cm^{-1} (parallel dichroism) and 1550 cm^{-1} (perpendicular dichroism).

Based on these observations, some criteria for differentiation between parallel and antiparallel folded polypeptide chains have been proposed. Both conformations have an amide I band with perpendicular dichroism at $1630 \pm 15\text{ cm}^{-1}$. The amide I band with parallel dichroism at 1695 cm^{-1} occurs only in antiparallel chains and is characteristic for these conformations. The presence of a band at 1630 cm^{-1} with perpendicular dichroism and the absence of a band at 1695 cm^{-1} suggests the existence of parallel folded chains. These conclusions are supported by the presence of a second amide I band at 1645 cm^{-1} .

Table II-226 shows frequencies of amide I and amide II bands and dichroism in some polypeptides and proteins with extended chains.

Table II-226 Frequencies of amide I and amide II bands (cm^{-1}) in extended conformations [11]

| Substance | Amide I | | Amide II | |
|--|-----------------|--------------------|-----------------|--------------------|
| | Dichroism π | Dichroism σ | Dichroism π | Dichroism σ |
| Horse hair | 1645 | 1630 | 1530 | 1550 |
| Silk (<i>Bombyx mori</i>) | 1695 | 1634 | 1520 | |
| Polyglycine I | 1685 | 1632 | 1530 | (1550)* |
| Poly- γ -methyl-L-glutamate | 1692 | 1627 | 1521 | |
| Poly-L-alanine | 1695 | 1635 | 1520 | |
| Sodium poly- α -L-glutamate (β')** | 1691 | 1625 | 1525 | |
| N-deutero sodium poly α L. glutamate (β')** | 1680 | 1620 | | |
| Poly-L-lysine \cdot HCl | 1690 | 1625 | | |

* Impurity.

** β' -Forms present when humidity is below 10% [41a]

2. *Helicoidal forms (α -helix)*. Calculated values for frequencies of the α -helix, the fundamental structure of proteins and polypeptides are shown in Table II-225. It is to be expected that in this conformation both components of the amide I band (parallel and perpendicular) would occur at ca. 1650 cm^{-1} . The parallel amide II band occurs at ca. 1520 cm^{-1} and the perpendicular one at ca. 1550 cm^{-1} .

It has been shown that in poly- γ -benzyl-L-glutamate the angle between the direction of the transition moment in amide I and amide II bands and the axis of the helix is $29-34^\circ$ and $75-79^\circ$, respectively.

Spectra of oriented films of poly- γ -benzyl-L-glutamate (Fig. II-108) and poly- α -L-glutamic acid in helicoidal conformation (recorded in water and dioxane) show parallel and perpendicular amide I and amide II bands of the α -helix (Table II-227) [11].

Table II-227 Frequency of amide I and amide II bands (cm^{-1}) in α -helicoidal forms [41]

| Substance | Amide I band | | Amide II band | |
|------------------------------------|-----------------|--------------------|-----------------|--------------------|
| | Dichroism π | Dichroism σ | Dichroism π | Dichroism σ |
| Poly- γ -benzyl-L-glutamate | 1650 | 1652 | 1516 | 1546 |
| Poly- α -L-glutamic acid | 1650 | 1650 | 1515 | 1550 |
| Elephant hair | 1660 | 1660 | 1615 | 1545 |
| Horse hair | 1650 | 1645 | 1620 | 1550 |
| Epidermis | 1655 | 1655 | 1620 | 1545 |

Older observations showing that the 1630 cm^{-1} band of the extended form has a larger dichroism than that of the 1650 cm^{-1} band of the α -helical form are because in the latter case the band is split into two components with opposite dichroism whereas in the former case there is a single band with σ -dichroism.

Studies of infrared spectra of helical polypeptide chains show that in the α -form the helix is preferentially oriented in the same direction as the stretching vibration and the N-H and C=O bonds are parallel to the helix axis. For example, in poly- γ -benzyl glutamate [44], the νNH frequency (3292 cm^{-1}) and the $\nu\text{C=O}$ frequency (1653 cm^{-1}) show parallel dichroism. The NH deformation band (1519 cm^{-1}) shows perpendicular dichroism. The ester νCO band (1750 cm^{-1}) does not show any dichroism.

3. *Random forms.* In these forms the amide I and amide II bands occur at 1660 and 1535 cm^{-1} .

Studies performed with polarized radiation have shown that the solvent used in film preparation can favor one form over the other. In poly-D,L-alanine, the extended β -form is favored by cresol and in poly- γ -methyl-L-glutamate and in the copolymer γ -methyl-L-glutamate-D, L-phenylalanine, this form is favored by formic acid. If the copolymer γ -methyl-L-glutamate-D,L-phenylalanine (1:1) is prepared in cresol, the α -helix is favored (Fig. 11-109).

Insulin has an α -helical conformation when the film is prepared in cresol ($\nu\text{CO } 1660\text{ cm}^{-1}$, dichroism σ) and an extended β -form in formic acid [45, 46].

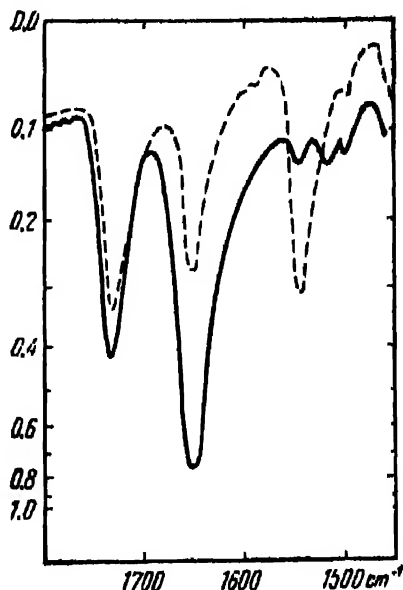


Fig. 11-108 Dichroism of bands in the spectrum of poly- γ -benzyl-L-glutamate (oriented form from chloroform solutions). Solid line - electric vector of the polarized radiation parallel to the direction of orientation; dotted line - electric vector perpendicular to the direction of orientation [41].

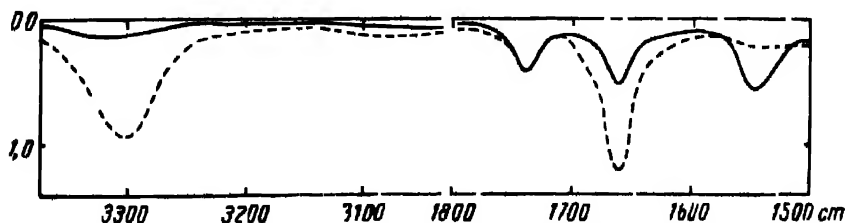


Fig. 11-109 Infrared spectrum of poly- γ -methyl-L-glutamate and D,L-phenylalanine 1:1, film from *m*-cresol. Solid line - electric vector of the perpendicular polarized radiation; dotted line - electric vector of the parallel polarized radiation.

However, in some cases the behavior of polypeptides is independent of the nature of the solvent (e.g. in tryptophan bands show the same dichroism in various solvents). Consequently, results obtained in these studies have to be interpreted with caution.

Polarized radiation enables the study in the infrared of $\alpha \rightarrow \beta$ -transformations of fibers as a function of pH, solvent, humidity, mechanical extension, etc.

By varying the pH and the humidity of poly- α -L-glutamate (sodium salt) and of poly- α -L-glutamic acid, it has been shown that the transformation α -helix \rightleftharpoons non-helix is reversible [17]. The spectrum of an oriented film of poly- α -L-glutamic acid [48] prepared in dioxane-water is characteristic for polypeptides with an α -helicoidal structure [44]. The ν NH band (3300 cm^{-1}) and the ν CO band (1655 cm^{-1}) show parallel dichroism and the amide III band (1550 cm^{-1}) shows perpendicular dichroism. The strong band of the COOH group occurs at 1710 cm^{-1} , but it shows a weak dichroism. The absorption of the COO^- ion at 1575 cm^{-1} does not occur. In the sodium salt of poly- α -L-glutamic acid at pH 7.3, the dichroism is weak, but the spectrum is characteristic for β -polypeptides with an extended conformation (3300 cm^{-1} , σ ; 1655 cm^{-1} , π). The 1550 cm^{-1} band is shielded by the strong absorption of the COO^- ion). After acidification, dialysis, and lyophilization, the dioxane-water solution again shows the characteristic spectrum of the α -helix form. It has been observed (in the case of poly-L-lysine \cdot HCl) that the $\alpha \rightarrow \beta$ -transformation takes place simply by altering the humidity of the sample [49].

In solid poly- α -L-glutamate four forms corresponding to hydrated and dehydrated α and β forms have been observed. When the humidity falls, the β form appears and when it rises the spectrum is that of the α -form. The unionized acid exists in the α -form at any degree of humidity [47].

Dichroism studies in poly-L-serine show that this polypeptide occurs in aqueous solution in a random or coil form. The fact that on deuteration the amide I band remains at 1658 cm^{-1} (cf. $1610 - 1645\text{ cm}^{-1}$ in the α -helix form) shows that the random form is much more likely. In solid poly-O-acetyl-L-serine, the spectrum shows an extended β -structure with antiparallel chains [50].

In simple dipeptides, results obtained with infrared spectroscopy agree with those obtained by X-ray studies [51].

c. **Deuteration.** Valuable information regarding the secondary structure of proteins and polypeptides has been obtained from studies in D_2O [52-62]. The kinetic analysis of the isotope exchange reaction of insulin [53], ribonuclease, and myoglobin [54] in D_2O has shown that these molecules have two types of hydrogen atoms; some which are readily replaceable by deuterium and others which do not undergo exchange. The kinetic results are supported by studies of infrared spectra of some solid proteins. From variations of the ν NH band at 3300 cm^{-1} , the nature and number of hydrogen bonds in the macromolecule have been evaluated [54].

In the case of fibrous proteins, for example, α -keratin, it has been observed that the macromolecule in the native state is not sensitive to isotope exchange

in D_2O . Only when some hydrogen bonds are destroyed are there indications for H-D exchange [54]. The conclusion is that the hydrogen atoms resisting exchange belong to the organized structure of the macromolecular fiber.

By observing the variation of the optical density ratio of amide II and amide I bands with time in proteins dissolved in D_2O , it has been shown that the deuteration time required to achieve equilibrium is the same for many proteins [57]. The diagram in Fig. II-110 shows that isotope exchange is fast during the first minutes, then it slows down in going toward equilibrium. The first phase is attributed to deuteration of the random region of the polypeptide chain [57]. The region undergoing slow deuteration is attributed to amide hydrogen atoms from the helicoidal portion of the chain or to other types of strong bonds. After 24 hours a certain amount of amide hydrogen atoms still remains unchanged.

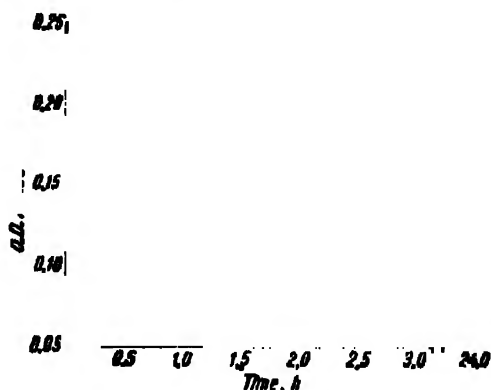


Fig. II-110 Deuteration rate of chymotrypsin (5% in D_2O) [57].

On heating the isotope exchange goes to completion. The portion of the molecule resisting II-D exchange is the hydrophobic region with very strong hydrogen bonds.

Table II-228 shows the amount of amide hydrogen resisting isotope exchange (HARIE) as a function of pD. The values obtained in the infrared are higher than those obtained by the optical rotatory dispersion method.

γ -Globulin has a small amount of hydrogen resisting isotope exchange, whereas in insulin about half the hydrogen atoms are involved in strong hydrogen bonds located in hydrophobic regions.

Ribonuclease [58] shows a phenomenon which has not been observed in insulin and poly-D, L-alanine. Part of the hydrogen does not undergo deuteration unless the natural structure of the protein has been perturbed. The 245

Table II-228 Amount of amide hydrogen resisting isotope exchange

| Protein | pD | HARIE, % | |
|------------------------|-------|--------------|-------------|
| | | after 10 min | after 24 hr |
| Insulin | 2 | 60 | 12 |
| Ovalbumin | 5 | 50 | 20 |
| Chymotrypsin | 4.5 | 43 | 15 |
| Beef plasma albumin | 5 | 40 | 5 |
| Ribonuclease | 4.5 | 35 | 12 |
| β -Lactoglobulin | 5-5.5 | 25 | 10 |
| Chymotrypsin | 4 | 20 | 10 |
| Trypsin | 4 | 14 | 5 |
| γ -Globulin | 4 | <10 | <10 |

replaceable hydrogen atoms in insulin are divided into four categories: 175 are rapidly replaced, 25 are slowly replaced at 0°, 25 are replaced at 38°C in 24 hours, and 20 cannot be replaced even at 38°C. The last 20 can be replaced only at the transition point (60°C and *pH* 4.8).

The same phenomenon has been observed in other proteins: β -lactoglobulin, chymotrypsinogen, sperm myoglobin, and serum albumin.

Studies of infrared spectra [59] have shown that the 20 hydrogen atoms not undergoing isotope exchange are involved in hydrogen bonds with nitrogen rather than with oxygen atoms. By comparing the spectrum of ribonuclease- D_2O deuterated below the transition temperature with that of completely deuterated ribonuclease above this temperature, it can be seen that in ribonuclease- D_2O the 20 hydrogen atoms are involved in bonding with nitrogen, the same as in poly- γ -benzyl-L-glutamate [38]. The interpretation of protein spectra is based on deuteration studies of polypeptides of known structure and conformation (e.g., poly-D,L-alanine with its 30 amino acid residues in a helical conformation) [51, 60].

In the case of poly- α -L-glutamic acid [57] the amide II band at 1550 cm^{-1} has been chosen for studies. It lies in a region of weak D_2O absorptions and is more isolated than the νNH band occurring at 3000 cm^{-1} . On deuteration the band shifts to 1450 cm^{-1} [61]. The isotope exchange can be followed by measuring the rate at which the optical density of the 1550 cm^{-1} band decreases. It has been shown that unionized poly- α -L-glutamic acid exists in the α -helix form both in the solid state and in water-dioxane solution. The sodium salt

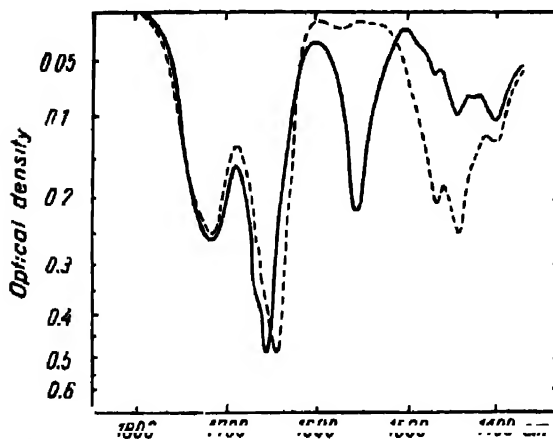


Fig. 11-111 Infrared spectrum of poly- α -L-glutamic acid. Solid line — undeuterated; dotted line — completely deuterated (5% in 1:1 dioxane - D_2O) [57].

has a random conformation which, however, can be oriented so as to have a β -conformation in the solid state. Consequently, the amide I band is not altered on deuteration. The amide II band vanishes, being replaced by the 1450 cm^{-1} band (Fig. 11-111).

The rate of exchange of the amide hydrogen atoms is slower in the acid (α -helix) than in the sodium salt (random).

Complete deuteration of poly- α -L-glutamic acid (with 100% α -helix structure as established by optical rotatory dispersion) takes place in 24 hours at *pD* = 4.2, whereas in the sodium salt the exchange takes place in 10 min. At *pD* 3.5 a band occurs at 1705 cm^{-1} because of interaction of terminal COOH groups in side chains. Deuteration is very slow at 50° (it is not complete even after 168 hr), but it is fast at 60°C.

In copolymers of L-glutamic acid-L-lysine with a partially random and partially α -helicoidal conformation [63], the rate of isotope exchange agrees with data obtained by the ORD method [37, 38, 56, 57].

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CHAPTER 12

AROMATIC HETEROCYCLIC COMPOUNDS

In spectroscopy, as well as in organic chemistry [1] separate treatment of aromatic heterocyclic compounds is justified by their special properties*. On replacing a CH group in benzene by a heteroatom (oxygen or nitrogen), the mass effect is relatively small and the electronic distribution, the essential factor which determines force constants, is practically unchanged. The infrared spectra of the two classes of compounds show many similarities. As in benzene, ring substitution is accompanied by characteristic absorptions. Some of them are independent of the nature of the substituent, whereas others are affected by its electronic effects. Finally, the difference in polarity between five- and six-membered heteroatomic rings (determined by different ways of generating the aromatic sextet) has a characteristic effect on the corresponding infrared spectra.

Spectra of fundamental monoheteroatomic aromatic heterocyclic compounds are described in the following sections.

a. Five-membered ring monoheteroatomic compounds

Parent compounds in this class have a planar pentagonal skeleton. The presence of the heteroatom results in a C_{2v} symmetry of the system. Furan and thiophene have 21 vibration modes each. Pyrrole with one extra atom has 24 vibration modes. Figure II-112 shows the 24 fundamental vibration modes in C_{2v} symmetry. In furan and thiophene vibration modes ν_9 , ν_{13} , and ν_{21} corresponding to the three degrees of freedom of the hydrogen atom attached to nitrogen are absent [2-4].

Assignments of fundamental vibrations for furan [5], thiophene [6], and pyrrole [4] are shown in Table II-229.

b. Six-membered ring monoheteroatomic compounds

Six-membered ring aromatic heterocyclic compounds formally result by replacing a CH group in benzene by a nitrogen or oxygen atom [1]. The aromatic sextet, formed by three pairs of π electrons (as in benzene), makes the structure and behavior of these molecules analogous to that of benzene.

The skeleton of the fundamental compounds, pyridine and the pyrilium cation, has a planar-hexagonal conformation. On replacing a CH group by a heteroatom, the D_{6h} symmetry of the benzene ring is reduced to C_{2v} , as in

* The other (nonaromatic) heterocyclic compounds are analogous to the corresponding acyclic compounds and are treated together.

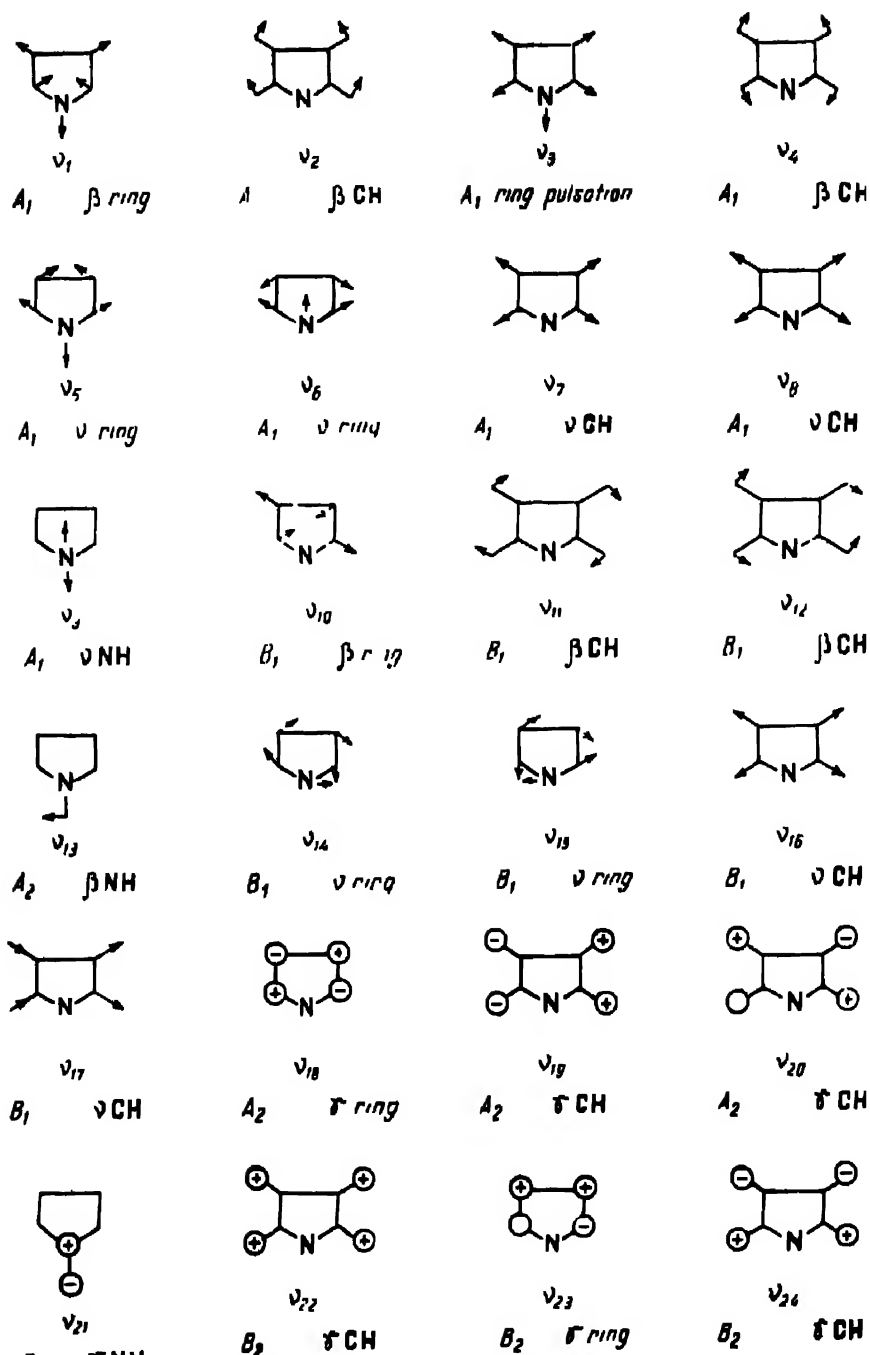
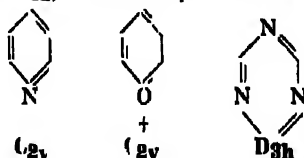


Fig. 11-112 Normal vibration modes of the pyrrole molecule.

Table II-229 Fundamental frequencies (cm^{-1}) in furan, thiophene, and pyrrole

| Assign- ment | Species | Vibration mode | Furan [5] | Thio- phene [6] | Pyrrole [4] | Assign- ment | Species | Vibration mode | Furan [5] | Thio- phene [6] | Pyrrole [4] |
|-----------------|---------|--------------------------|--------------|-----------------------|----------------|-----------------|---------|---------------------------|--------------|-----------------------|----------------|
| ν_8 | A_1 | $\nu\text{C}-\text{H}$ | 3124 | 3093 | 3183 | ν_{12} | B_1 | $\beta\text{C}-\text{H}$ | 1181 | 909 | 1015 |
| ν_7 | A_1 | $\nu\text{C}-\text{H}$ | (3124) | 2996 | 3100 | ν_{13} | B_1 | $\beta\text{N}-\text{H}$ | — | — | 1074 |
| ν_{17} | B_1 | $\nu\text{C}-\text{H}$ | 3163 | (3093) | (3133) | ν_9 | A_1 | ring pulsation | 995 | 832 | 1144 |
| ν_{18} | B_1 | $\nu\text{C}-\text{H}$ | (3163) | 2996 | 3111 | ν_{24} | B_2 | $\gamma\text{C}-\text{H}$ | 838 | (832) | 838 |
| ν_9 | A_1 | $\nu\text{N}-\text{H}$ | — | — | 3400 | ν_{20} | A_2 | $\gamma\text{C}-\text{H}$ | 1030 | 748 | 652 |
| ν_{15} | B_1 | ν ring | 1586 | 1590 | 1530 | ν_{22} | B_2 | $\gamma\text{C}-\text{H}$ | 744 | 710 | 735 |
| ν_6 | A_1 | ν ring | 1490 | 1404 | 1467 | ν_{19} | A_2 | $\gamma\text{C}-\text{H}$ | 680 | 686 | 711 |
| ν_{14} | B_1 | ν ring | 1400 | 1252 | 1418 | ν_{21} | B_2 | $\beta\text{N}-\text{H}$ | — | — | 565 |
| ν_5 | A_1 | ν ring | 1384 | 1358 | 1384 | ν_{10} | B_1 | γ ring | 871 | 872 | 867 |
| ν_{11} | B_1 | $\beta\text{C}-\text{H}$ | 1268 | 1290 | 1046 | ν_1 | A_1 | β ring | 720 | 604 | 711 |
| ν_4 | A_1 | $\beta\text{C}-\text{H}$ | 1140 | 1079 | 1237 | ν_{23} | B_2 | γ ring | 601 | 453 | 649 |
| ν_3 | A_1 | $\beta\text{C}-\text{H}$ | 1067 | 1032 | 1076 | ν_{18} | A_2 | γ ring | 550 | 565 | 618 |

monosubstituted benzenes. Polyheteroatomic compounds can have intermediate symmetries (1, 3, 5-triazine, D_{3h}) or lower symmetries [7, 8].



Pyridine and the pyrilium cation have a symmetry axis C_{2v} passing through the heteroatom and two perpendicular planes of symmetry σ_{xz} , σ_{yz} . Their intersection is the C_{2z} axis.

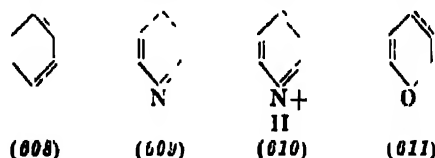
The 27 vibration modes are distributed as follows: 10 A_1 , 9 B_1 , 5 B_2 , active in the infrared, and 3 A_2 active in Raman. The assignments are shown in Table II-230.

Table II-230 Fundamental frequencies (cm^{-1}) in benzene, pyridine, and pyrilium cations [9]

| Assign- ment | Species | Vibration mode | Benzene | Pyri- dine | Pyri- lium | Assign- ment | Species | Vibration mode | Benzene | Pyri- dine | Pyri- lium |
|-----------------|---------|--------------------------|---------|---------------|---------------|-----------------|---------|---------------------------|---------|---------------|---------------|
| ν_8 | A_1 | $\nu\text{C}-\text{H}$ | 3062 | 3054 | 3062 | ν_{15} | B_1 | $\beta\text{C}-\text{H}$ | 1147 | 1148 | 1170 |
| ν_{7b} | B_1 | $\nu\text{C}-\text{H}$ | 3047 | 3036 | 3016 | ν_{16b} | B_1 | $\beta\text{C}-\text{H}$ | 1037 | 1085 | 1060 |
| ν_{13} | A_1 | $\nu\text{C}-\text{H}$ | 3060 | 3054 | 3062 | ν_{18a} | A_1 | $\beta\text{C}-\text{H}$ | 1037 | 1068 | 1039 |
| ν_{10a} | A_1 | $\nu\text{C}-\text{H}$ | 3080 | 3036 | 3016 | ν_1 | A_1 | ring pulsation | 992 | 992 | 995 |
| ν_{20b} | B_1 | $\nu\text{C}-\text{H}$ | 3080 | 3063 | 3124 | ν_{12} | A_1 | $\nu\text{C}-\text{C}$ | 1010 | 1030 | 1021 |
| ν_{2a} | A_1 | ring | 1596 | 1583 | 1620 | ν_5 | B_2 | $\gamma\text{C}-\text{H}$ | 985 | 942 | 958 |
| ν_{2b} | B_1 | $\nu\text{C}-\text{C}$ | 1596 | 1572 | 1557 | ν_{10b} | B_2 | $\gamma\text{C}-\text{H}$ | 849 | 886 | 850 |
| ν_{19a} | A_1 | $\nu\text{C}-\text{C}$ | 1485 | 1482 | 1474 | ν_{11} | B_2 | $\gamma\text{C}-\text{H}$ | 671 | 700 | 652 |
| ν_{19b} | B_1 | $\nu\text{C}-\text{C}$ | 1485 | 1439 | 1412 | ν_{2a} | A_1 | β ring | 606 | 605 | 582 |
| ν_{14} | B_1 | $\nu\text{C}-\text{C}$ | 1309 | 1375 | 1387 | ν_{2b} | B_1 | $\nu\text{C}-\text{C}$ | 606 | 652 | 652 |
| ν_9 | B_1 | $\beta\text{C}-\text{H}$ | 1326 | 1218 | 1216 | ν_{4b} | B_2 | γ ring | 702 | 749 | 779 |
| ν_{2a} | A_1 | $\beta\text{C}-\text{H}$ | 1178 | 1218 | 1216 | ν_{16b} | B_2 | γ ring | 405 | 405 | 400 |

Vibration modes 7*a*, 9*b*, and 17*b* of the additional hydrogen atom in benzene have been excluded from Table II-230. Also excluded are fundamentals 10*a*, 16*a*, and 17*a* of the A_2 species, active only in Raman.

The vibrational analogy between benzene and pyridine is also valid for the pyrilium cation [9]. In the series benzene, pyridine, pyridinium cation, pyrilium cation an increase in $\delta C-C$, $\gamma C-C$, and $\delta C-H$ deformation frequencies and a decrease in $\gamma C-H$ deformation frequencies have been observed.



The ring C-C stretching vibrations 8*a*, 8*b*, 19*a*, and 19*b*, degenerate and forbidden in the infrared spectrum of benzene (**D_{6h}**) are active in monoalkylbenzenes (Fig. II-52). The frequency difference between components *a* and *b* is 0–10 cm^{-1} . In the heterocyclic series with C_{2v} symmetry, the separation between ν_{8a} and ν_{8b} bands increases steadily from (608) to (611) by 0, 11, 30, 63 cm^{-1} . In pyrilium salts, $\Delta\nu$ is the largest.

In pyridine the intensities of ν_{8a} and ν_{19a} bands are higher than those of ν_{8b} and ν_{19b} bands, whereas in the pyrilium cation the ratio is reversed.

Vibrations ν_{20a} and ν_{20b} , degenerate in benzene, are also split. In the (608)–(611) series the distance between the two components increases from 47 cm^{-1} in pyridine (Fig. II-113 *a*) to 108 cm^{-1} in the pyrilium cation [9] (Fig. II-113*b*) (Table II-230).

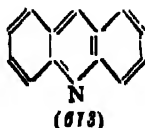
Quinoline. The spectrum of quinoline (612) [10, 11] and of substituted derivatives [12] has been interpreted by analogy with naphthalene and ortho-disubstituted benzenes.



Of the nine theoretical bands ($\nu C-C$ ring), eight occur in the 1350–1620 cm^{-1} region [11]. $\beta C-H$ and $\gamma C-H$ deformation vibrations between 800 and 1350 cm^{-1} depend on the number and position of substituents [12,13].

Frequencies and apparent intensities ($\epsilon^{(a)}$) in quinoline are: 1622 (25), 1598 (35), 1576 (40), 1506 (110), 1437 (10), 1453 (10), 1435 (15), 1396 (15), 1374 (25).

Acridine and derivatives. Spectra of acridine (613) and substituted derivatives [14] show three bands in the $\nu C-H$ region, at 3030 ± 10 , 3066 ± 7 , and $3077 \pm \text{cm}^{-1}$.



Three bands (combination or overtones) are characteristic. They occur in the saturated νCH region at 2950 ± 10 , 2917 ± 3 , and $2848 \pm 3 \text{ cm}^{-1}$.

In the $1360\text{--}1630 \text{ cm}^{-1}$ region acridines show 7–9 bands of appreciable intensity. Their position and intensity vary with the nature and position of

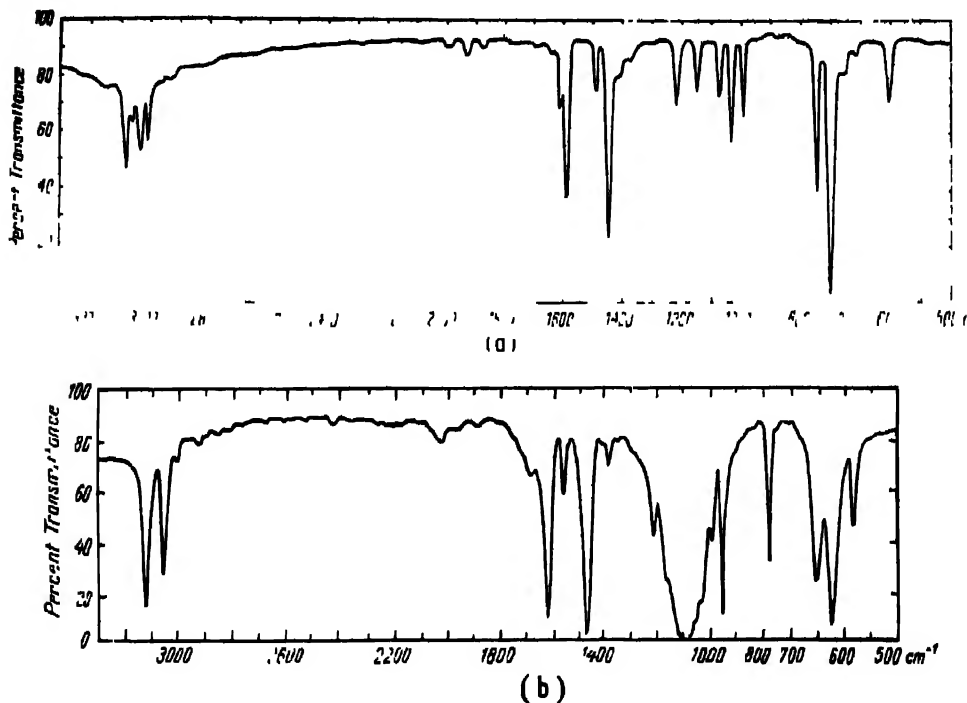


Fig. II-113 (a) Infrared spectrum of pyridine and (b) pyrilium perchlorate.

substituents in the heterocyclic ring. The mean frequencies of the seven bands occurring in acridines substituted in the 9-position are: 1628 ± 3 , 1603 ± 7 , 1516 ± 2 , 1519 ± 1 , 1161 ± 2 , 1431 ± 3 , and $1397 \pm 2 \text{ cm}^{-1}$ [11, 15].

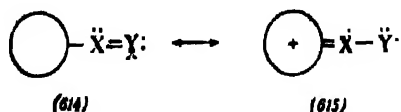
The ring pulsation gives rise to two characteristic bands at ca. 1000 cm^{-1} .

c. *The effect of the heterocyclic ring on the vibrations of the functional group*

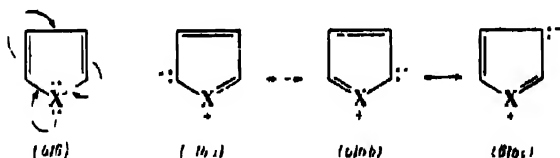
In aromatic heterocyclic systems, the π electrons of the aromatic sextet are conjugated with p or π electrons of the functional group. Alterations in bond order, hence in frequency of the functional group (cf. the same functional group attached to a benzene ring) reflect the electron-releasing or electron-attracting properties of the heterocyclic ring.

Keeping the functional group (e.g., COR, CH₂O, COOR, COOH) constant and varying the heterocyclic ring, it can be seen that five-membered rings (614) are electron donors, favoring shifts toward structure (615). This results

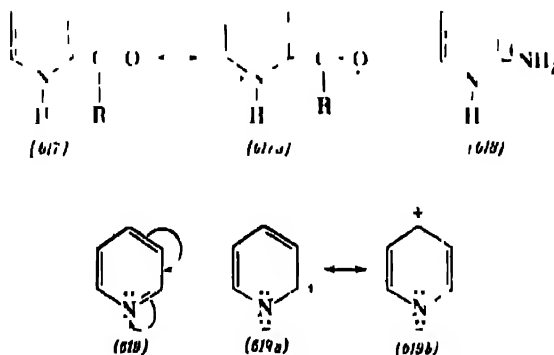
in a decrease in ν_{CO} frequencies. Six-membered rings raise the frequency; consequently they are electron acceptors. Frequency shifts depend on the electronegativity of the heteroatom in both cases.



The difference in behavior is because of a different electron distribution in five-membered rings, cf. six-membered rings. In five-membered rings (616) the heteroatom has a positive polarity (a larger contribution of dipolar structures enriched in electrons in the 2- and 5-positions).



The contribution of structures (616a) and (616b) increases in the order O, N, S, paralleling the decrease in electronegativity of the heteroatom. Consequently, the electron-releasing character of the ring will be stronger in the α -position than in the β -position and will increase in the order O, N, and S. The bond order of multiple bonds in functional groups decreases. Thus the frequencies of the corresponding bonds (617a) decrease.



Electron-releasing substituents (OH , NH_2) with a $-I$ effect increase the electron density by means of structures such as (618).

In six-membered ring heterocyclic compounds (619), the $-I$ and $-E$ effect of the heteroatom result in a general decrease in electron density which is more significant in the α - and γ -positions (619a, 619b). The electron-attracting effect of the ring on the functional group is felt stronger in the α - and γ -posi-

tions than in the β -position. In six-membered heterocycles substituted with CHO, COCH₃, COOR groups, frequencies of double bonds in functional groups are 6–20 cm⁻¹ higher cf. analogous compounds in the benzene series. The effect is stronger in compounds substituted in the γ -position than in the β -position [2, 7, 16, 17].

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APPENDIX


CHARACTERISTIC GROUP FREQUENCIES

Appendix I

| | | cm ⁻¹ | | | | | | | | | | | | | | | | | |
|--------------|---|------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|-----|-----|-----|
| | | 4000 | 3600 | 3400 | 3200 | 3000 | 2800 | 2600 | 2400 | 2200 | 2000 | 1800 | 1600 | 1400 | 1200 | 1000 | 800 | 600 | 400 |
| Alkanes | $\text{CH}_3 -$ $\text{CH}_2 -$ $\text{CH} -$ $\text{C}_2\text{H}_5 -$ $\text{CH}_3(\text{CH}_2)_2 -$ $(\text{CH}_3)_2\text{CH} -$ $(\text{CH}_3)_3\text{C} -$ | | | | | | | | | | | | | | | | | | |
| Cycloalkanes | $(\text{CH}_2)_n \begin{cases} n \geq 5 \\ n = 4 \\ n = 3 \end{cases}$ $\text{C} - \text{H} \text{ bending}$ | | | | | | | | | | | | | | | | | | |
| Alkenes | $\text{CH}_2 = \text{CH} -$ $> \text{C} = \text{CH}_2$ $\text{RCH} = \text{CHR} \begin{cases} \text{trans} \\ \text{cis} \end{cases}$ $> \text{C} = \text{CH} -$ <i>Alkenes</i> | | | | | | | | | | | | | | | | | | |
| Acetylenes | $\text{C} \equiv \text{C} - \text{H}$ $\text{C} \equiv \text{C} -$ | | | | | | | | | | | | | | | | | | |
| Arenes | $\text{C}_6\text{H}_5 - \text{X}$ $\text{C}_6\text{H}_4\text{X}_2 \begin{cases} \text{ortho} \\ \text{meta} \\ \text{para} \end{cases}$ $\text{C}_6\text{H}_3\text{X}_3 \begin{cases} 1,2,3 \\ 1,2,4 \\ 1,3,5 \end{cases}$ $\alpha - \text{C}_{10}\text{H}_7\text{X}$ $\beta - \text{C}_{10}\text{H}_7\text{X}$ | | | | | | | | | | | | | | | | | | |

CHARACTERISTIC GROUP FREQUENCIES

(Continued)

| | cm^{-1} | |
|----------------------|---|---|
| Organic cations | 400 600 800 1000 1200 1400 1600 1800 2000 2200 2400 2600 2800 3000 3200 3400 3600 | Carbocations Oxocarbenium ions |
| Halogen compounds | | $\text{C}-\text{F}$ $=\text{C}-\text{F}$ $\text{C}-\text{Cl}$ $\text{C}-\text{Br}$ $\text{C}-\text{I}$ |
| Alcohols and Phenols | | $-\text{CH}_2-\text{OH}$ $>\text{CH}-\text{OH}$ $\geq\text{C}-\text{OH}$  $\left. \begin{array}{l} \text{equatorial} \\ \text{axial} \end{array} \right\}$ phenols |
| Ethers | | aliphatic aromatic acetal ketal epoxide |
| Sulfur compounds | | $\text{S}-\text{H}$ $\text{C}-\text{S}$ $\text{R}-\text{S}-\text{R}$ $>\text{SO}$ $>\text{SO}_2$ $-\text{SO}_3\text{H}$ $-\text{SO}_3^-\text{NH}_2$ |

CHARACTERISTIC GROUP FREQUENCIES

(Continued)

| | cm^{-1} | 400 600 800 1000 1200 1400 1600 1800 2000 2200 2400 2600 2800 3000 3200 3400 3600 |
|--------------------|---|---|
| Nitrogen compounds | <p>Alkyl - NO₂ Aryl - NO₂</p> <p>R-NO { monomeric dimer</p> <p>Primary amines { -CH₂-NH₂ >CH-NH₂</p> <p>Secondary amines { NH NH</p> <p>Tertiary amines { alkyl aryl</p> <p>Aliphatic aromatic</p> <p>-NH₃⁺ Cl⁻</p> <p>R₃N-O</p> <p>>C=NH</p> <p>>C=N-C<</p> <p>-N=C<</p> <p>RN₃</p> <p>-N=N-</p> <p>>C=N=N</p> <p>>C=NOH</p> <p>Quinoxaline</p> <p>O₂N-O-R</p> <p>ON-O-R</p> | |
| Carbonyl compounds | <p>R-CHO { aliphatic aromatic</p> <p>R₂C=O { aliphatic aromatic</p> | |

CHARACTERISTIC GROUP FREQUENCIES

(Continued)

| | cm ⁻¹ | 400 600 800 1000 1200 1400 1600 1800 2000 2200 2400 2600 2800 3000 3200 3400 3600 |
|----------------------------------|---|---|
| Carboxylic acids and derivatives | <p>-COOH -COO⁻</p> <p>R-COCl</p> <p>Esters { butyrate, acetates formates aromatic</p> <p>Anhydrides { normal cyclic</p> <p>Amides { -CONH₂ -CONHR -CONR₂</p> | |
| Carbonic acid derivatives | <p>-R-C≡N R-N≡C-O Cl-COOR OC(OR)₂</p> | |

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